

ROTATIONAL STRUCTURE IN THE SPECTRA OF DIATOMIC MOLECULES

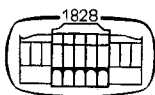
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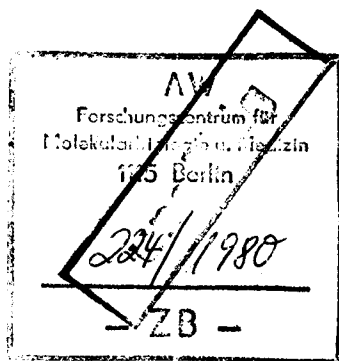
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PREFACE

It is mainly since the early 1920's that the rotational spectra of diatomic molecules have been investigated. During this time it has become clear how deeply rooted are the connections between these spectra and the internal structure of the molecules and how important is the information they give about molecular architecture. It has become evident that these spectra are, say, coded messages from the molecules in secret writing and that to decipher these messages it is necessary to determine experimentally the position and intensity of the spectral lines and to establish the theoretical laws governing the spectra. Although the fundamental investigations about rotational spectra were published in the third and fourth decades of this century and the fundamental theory can be found in a number of excellent books, it seems appropriate and necessary to collate this material in the form of a unified system and to complete this system by adding new elements. This is especially true with respect to the formulas of intensity distribution, a systematic collection of which is in growing demand by physicists and astronomers. The author's aim is to meet this demand by the present book.

There are certain advantages and some limitations inherent in this task. First it is important to see that the rotational part of the spectrum is a relatively narrow band compared with the vibrational and electron spectra of a molecule. It is, however, just this limitation that renders it possible to penetrate this special field more profoundly than can be done in more comprehensive works. Still, despite the restrictedness of this field it has not been the author's intention to achieve completeness either on the theoretical side or in experimental details. The theoretical treatment is restricted to phenomena for which progress has made possible a unified, and in many cases novel, approach, or the stopping of gaps. It follows that those problems about which there is nothing new and which are covered in other, excellent books are omitted here. Of course, it would be impossible to achieve completeness on the experimental side, and only the most characteristic experimental cases are mentioned, to illustrate theoretical points.

Still, the task has proved to be extensive and complicated owing to the steady and fast progress in the field. Half of the works referred to in this book have been published since the middle of this century. This period has been the time for the elaboration of details, the completion of theories, and for modern applications, making it possible to write a review upon unified viewpoints. (The present volume comprises the results up to the end of 1966.)

It is the writer's hope that the present book will be useful to both theoretical and experimental research workers who want complete and unified information concerning the rotational structure in spectra.

It is the pleasant duty of the writer to express his acknowledgement for all the help and cooperation during the preparation of the manuscript. Sincere thanks are due to Dr G. Herzberg whose invitation for a three-month stay at the National Research Council (Ottawa) provided the writer with an excellent opportunity to bring this book to fruition. He is also grateful to Professor A. Budó (Szeged) and Professor R. Gáspár (Debrecen) who were kind enough to read the manuscript and offer important advice.

Budapest 1969

I. Kovács

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INTRODUCTION

GENERAL REMARKS ON OBSERVED SPECTRA

The first studies on spectra made it clear that, in addition to the continuous and line spectra, there are spectra with an entirely different structure. Spectrographs of lower resolution showed bands in the latter type of spectrum that extend over a certain width, and most of them are sharply limited on one side instead of being composed of separate sharp lines throughout. Such spectra are called *band spectra*. In contrast with the line spectra that are generated by the atoms, the sources of band spectra are the molecules. The study and interpretation of band spectra, or *molecular spectra*, has undergone a rapid progress since the 1930's, which has proved these spectra to be the most important source of information about molecular structure.

Upon examining the band spectra with a spectrograph of higher resolving power it is found that the bands are composed of many lines, spaced at regular intervals, the number of which frequently exceeds one hundred. The sharp limit of the band, the band head, is made up of a crowding of lines at one end of the band. The assembly of a number of *lines* gives rise to a *band*; the bands having similar structure and behaviour upon changes in external conditions (e.g. pressure in the discharge tube, temperature, etc.) group in a *band system*. In the complete spectra of molecules, a number of such band systems are normally observed. In some spectra the band systems contain only a few bands, whereas in others the number of bands can be more than one hundred. (See Fig. 1. Intr.)

In most molecular spectra the *threefold structure* (line-band-band system) can be easily recognized; in certain spectra, however, e.g. in the *many-line* spectrum of the H_2 molecule, no bands can be seen at all, only a very great number of lines, to which a continuous spectrum attaches rather frequently.

The molecular spectra, characterized briefly above, are found in the visible and ultraviolet part of the spectrum. The spectrum of many molecules extends, however, into the *near-infrared* (below 20 micron wavelength) or the *far-infrared* (above 20 microns). The long-wave infrared part of the spectrum is called the *rotational spectrum*; the short-wave infrared part is known as the *vibrational-rotational spectrum*, and the visible and ultraviolet parts are called *electronic band spectra*. These denominations—as will be seen later—are related to the various modes of motion of the molecule.

There are several problems of an experimental and technical nature that arise on producing and investigating spectra, e.g. the design and construction of spectral apparatus, spectral photography and other recording techniques used in the infrared region, conditions of excitation of the spectra, recognition of the molecule producing the spectrum, separation of the different band systems, measurement of wavelength and intensity, and so on. These topics cannot be dealt with here; let it be sufficient to note that, in

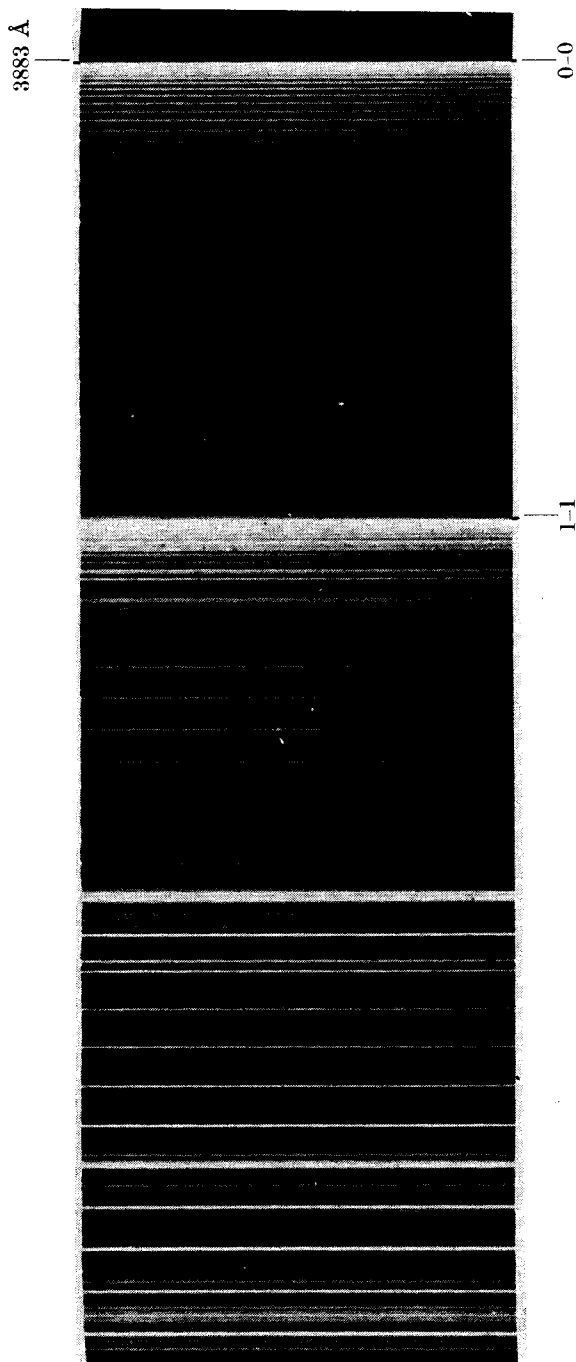


Fig. 1. (Intr.) Rotational structure of some emission bands in the violet band system of CN molecule.

the case of molecular spectra, both *emission* and *absorption* spectra are of great importance. The former type of spectrum can be produced, as is well known, when a molecular gas is excited (e.g. by electric discharges); the excitation causes the emission of a light of a certain wavelength; the latter type of spectrum is observed when the molecular gas absorbs certain wavelengths from a light having a continuous spectrum.

Spectral lines can be characterized by their intensity and position in the spectrum. The position can be expressed in terms of directly measurable wavelength λ , or rather by the reciprocal of the wavelength, called the wave-number ν (number of waves per cm), i.e. the unit of wavenumber is cm^{-1} . For example, if a spectral line's wavelength is $\lambda = 5,000$ Ångströms ($= 5,000 \times 10^{-8}$ cm), then its wavenumber is $20,000 \text{ cm}^{-1}$ (in other words, 20,000 waves can be accommodated within the space of 1 cm).

With experience, a table can be constructed from certain quantities describing certain properties of the molecule, where the wavenumber of any spectral line will be the difference between two tabulated values, i.e.

$$\nu = F' - F'' \quad (1)$$

The tabulated quantities F are called *spectral terms*. For the spectral terms of the simplest spectra there is a well known empirical formula that can be written in the following form:

$$F = F_{e1} + \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 - \dots + B_v J(J + 1) - D_v J^2(J + 1)^2 + \dots \quad (2)$$

where

$$B_v = B_e - \alpha_e(v + 1/2) - \dots; \quad D_v = D_e + \gamma_e(v + 1/2) \quad (3)$$

The symbols v and J are integer-valued variables; the rest of the symbols denote constants.

In the simplest case the wavenumber of a spectral line is the difference between two terms as said above. In such a case the first terms of the formula, F'_{e1} and F''_{e1} , are constants within a band system, whereas the second group of terms varies as v' and v'' , respectively, and describes the bands within the band system; this group is also constant within a band. Finally, the third group of terms, J' and J'' , respectively, describes the lines within the bands, the finest elements of the spectra. Therefore Equation (2), built from the previous three parts, expresses the threefold structure of the spectra.

The aim of spectral theory is to derive these formulas, to relate their coefficients to the known molecular constants, in order to interpret the threefold structure in a dynamical manner. This is dealt with in Chapter 1.

The last two term groups of the above formula lead to results in agreement with experiments only in the most simple cases. In the majority of the cases, relations that are much more complicated are found to be valid, these relations arising from the multiplying of molecular terms.

In Chapter 1 more general theoretical grounds are given for the interpretation of these multiplet molecular terms than would be absolutely

necessary for the theoretical explanation for (2); this then renders it possible to give in Chapter 2 such theoretically formulated relations for the *multiplet molecular terms* as are in agreement with experimental findings.

The knowledge of the term values is, however, not sufficient to characterize completely the spectral lines. Although the wavenumber of any spectral line can be produced as the difference of two terms, the difference of any two terms is not necessarily the wavenumber of an actual spectral line; i.e. the reverse of the above statement is not generally valid. Therefore, the above principles have to be complemented with various *selection rules* for determining the positive term differences that are real wavenumbers. *Intensity*, as has been mentioned earlier, is also a characteristic of a spectral line, actually as important as its wavenumber. In Chapter 3, therefore, term differences covering real spectral lines, and also the intensities deriving from these, will be established.

It has been observed in many spectra that the regular succession of the frequencies and intensities of spectral lines is upset for a single line or for several subsequent lines; the frequency and intensity of this line (or these lines) may substantially differ from the values deriving from the term formulas in Chapter 2 and the intensity formulas in Chapter 3. This phenomenon is called *perturbation* in the spectroscopical sense. Chapter 4 describes this phenomenon, and provides a theoretical interpretation, making use of the general results of Chapter 1.

For a better understanding of all these, it is useful for the reader to have a working knowledge of the experimental facts of molecular spectra and a detailed and thorough knowledge of quantum mechanics.

FOUNDATIONS OF A THEORY OF DIATOMIC MOLECULES

The interpretation of molecular spectra is based, as is that of the atomic spectra, on the two *Bohr* postulates, which have lately been verified by modern quantum theory. According to them, (i) a molecule can exist only in states of definite energies, in the stationary states; as long as the molecule is in one of these states, it does not emit or absorb light; (ii) light absorption or light emission is possible only as a result of a transition between two stationary states; the frequency $\bar{\nu}$ of the emitted or absorbed light is in relation with the respective energies, W' and W'' , of the higher and lower state as follows:

$$h\bar{\nu} = W' - W'' \quad (1)$$

where h is *Planck's* constant.

In the above fundamental relation, instead of the directly measurable wavelength of a line it is more advisable to use the frequency $\bar{\nu} = c/\lambda$ (where c is the velocity of light in vacuum) or to use the wavenumber, ν , in order to obtain data that are independent of a possible later correction of c :

$$\nu = \frac{\bar{\nu}}{c} \quad \text{or} \quad \nu = \frac{1}{\lambda} \quad (2)$$

By (1) and (2), the wavenumber of a line is

$$\nu = \frac{W'}{hc} - \frac{W''}{hc} \quad (3)$$

Upon comparing (3) with the expression (1) in the Introduction, it seems necessary to identify the corresponding terms of the two expressions. Accordingly, the positive quantities W/hc , being in effect energy values divided by a constant, can be called molecular terms. Hence,

$$F = \frac{W}{hc} \quad (4)$$

The first task in the interpretation of a spectrum is therefore to establish the terms, or in other words, the *energy levels* of the stationary states. In solving this problem it has proved useful to resort to certain simplified *molecular models* instead of considering the actual molecule. In this way it is possible to visualize the 'molecule' and to describe qualitatively some of its properties by means of the easy-to-grasp concepts of classical physics. In an effort to approximate the rather complicated motions of diatomic

molecules, three relatively simple models were combined. The first of these is the *stationary molecule*. Here a space-fixed system of nuclei is understood, with electrons orbiting around the nuclei. The second model is the *anharmonic oscillator*, and the third is the *symmetric top*. Thus the changes in the electronic configuration around the two nuclei, due to the energy level transitions of the electrons, give rise to the band systems; the bands within the band systems derive from the transitions between different vibrational states of the nuclei; and finally—since the nuclei not only vibrate but rotate as well—the transitions between the different rotational states give rise to the lines within the bands. The energy of the molecule is the sum of the energies of all these types of nuclear motion. Hence, the first part of Eq. (2) in the Introduction is, apart from the constant hc , the *electronic energy*; the second part is the *vibrational energy*, and the third part is the *rotational energy*.

In order to establish quantitative relationships, the methods of quantum theory and quantum mechanics will be applied to these models as well. For this reason, the wave equation of the molecule and its solution will be discussed first.

1.1. WAVE EQUATION AND ITS APPROXIMATE SOLUTION

The first research workers to attack the wave equation of diatomic molecules were Slater [199], Born and Oppenheimer [15] and Kronig [135]. They, however, did not take into account the electron spin, and therefore their results have only a limited validity. Van Vleck [211] and Kronig [6] were the first to discuss the wave equation complete with electron spin; our discussion will follow their reasoning.

The motion of the molecule is referred to a coordinate system x, y, z fixed in space. Disregarding the translatory motion of the molecule as a whole, as it engenders no part of the spectrum of the molecule, we consider the mass center of the nuclei as being at rest at the origin of the coordinate system x, y, z . Besides the coordinate system x, y, z we introduce another one (ξ, η, ζ) fixed to the molecule, with its origin likewise at the mass centre of the nuclei. The difference between the mass centre of the molecule and that of the nuclei will be omitted in the following discussion; owing to the small mass of the electrons, this omission does not essentially influence the results. As is well known, the position of a coordinate system fixed to a rigid body can be referred to by means of the three *Eulerian* angles ψ, θ, φ . The following relationships will then hold between the coordinates in the stationary and moving systems:

$$\begin{aligned} x &= (\xi \cos \varphi - \eta \sin \varphi) \cos \psi - [(\xi \sin \varphi + \eta \cos \varphi) \cos \theta - \zeta \sin \theta] \sin \psi \\ y &= (\xi \cos \varphi - \eta \sin \varphi) \sin \psi + [(\xi \sin \varphi + \eta \cos \varphi) \cos \theta - \zeta \sin \theta] \cos \psi \\ z &= (\xi \sin \varphi + \eta \cos \varphi) \sin \theta + \zeta \cos \theta \end{aligned} \quad (1)$$

The ζ axis coincides with the molecular axis; its positive sense is chosen so as to point from nucleus 2 towards nucleus 1.

In a coordinate system with a fixed point (the centre of mass) and a fixed direction (the direction of the internuclear axis, or rather the direction of the ζ axis) there is only one degree of freedom, that of rotation about the ζ axis. In this latter respect there are several possible choices. Kronig [135] uses a $\xi\zeta$ plane having a selected electron, in such a way that the ξ coordinate of the electron is positive. Later van Vleck [211] and Kronig [6] also placed the positive half of the ξ axis into the positive quadrant of the xy plane, with the consequence that, in Eq. (1), φ became zero. The angle of rotation about the ξ axis from the z axis to the ζ axis in the positive sense is denoted θ (Fig. 1.1), with $0 \leq \theta \leq \pi$. This angle is the same as ϑ in (1), i.e. $\vartheta = \theta$. The angle between the x axis and the projection of the ζ axis on to the xy plane, as measured in the positive sense about the z axis, is called ω ; i.e. $\varphi = \omega + \pi/2$.

Hence, (1) transforms into

$$\begin{aligned} x &= -\xi \sin \omega - (\eta \cos \theta - \zeta \sin \theta) \cos \omega \\ y &= \xi \cos \omega - (\eta \cos \theta - \zeta \sin \theta) \sin \omega \\ z &= \eta \sin \theta + \zeta \cos \theta \end{aligned} \quad (2)$$

or

$$\begin{aligned} \xi &= y \cos \omega - x \sin \omega \\ \eta &= z \sin \theta - (x \cos \omega + y \sin \omega) \cos \theta \\ \zeta &= z \cos \theta + (x \cos \omega + y \sin \omega) \sin \theta \end{aligned} \quad (3)$$

The positions of the electrons can be characterized in terms either of the space-fixed or of the molecule-fixed system.

Since Pauli [174] has introduced the electron spin, the wave equation of the molecule contains also the spin coordinates, as well as the positional coordinates, of the individual electrons. With the z axis or ζ axis, respectively, as a fixed direction in space, the electron spins are either parallel or antiparallel to that axis.

If α_k (β_k) denotes the parallel (antiparallel) orientation of the k th electron with relation to the z axis, and if α_k (β_k) denotes this orientation with respect to the ζ axis, the wave function can be written for f electrons as

$$\begin{aligned} &\psi_{s_1 \dots s_f}(x_1 \dots x_f, y_1 \dots y_f, z_1 \dots z_f, r, \theta, \omega) \\ &\psi_{\sigma_1 \dots \sigma_f}(\xi_1 \dots \xi_f, \eta_1 \dots \eta_f, \zeta_1 \dots \zeta_f, r, \theta, \omega) \text{ (case } a) \\ &\psi_{s_1 \dots s_f}(\xi_1 \dots \xi_f, \eta_1 \dots \eta_f, \zeta_1 \dots \zeta_f, r, \theta, \omega) \text{ (case } b) \end{aligned} \quad (4)$$

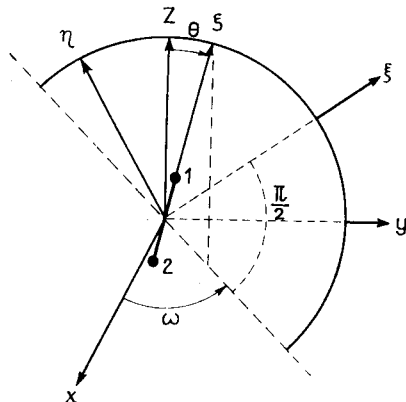


Fig. 1.1 Relation between space-fixed and molecule-fixed coordinate systems.

where each of s_1, \dots, s_f is either a or b , and each of $\sigma_1, \dots, \sigma_f$ is either α or β . Thus in each case 2^f wave functions are possible; owing to the interaction between the spins and orbital angular momenta of the individual electrons, it is the linear combinations of these wave functions that are usually encountered. The positional and spin coordinates of the electrons are expressed in the space-fixed coordinate system in the first case and in the molecule-fixed system in the second case. In the third case the positional coordinates are in the molecule-fixed system and the spin coordinates in the space-fixed system. Case a is used when the influence of the electron spin upon the motion of the molecule is greater than the influence of nuclear rotation; in the opposite situation case b is used.

On the basis of the above considerations, the wave equation of a molecule having moving nuclei takes the following form:

$$[\mathbf{H}(x_1, \dots, y_1, \dots, z_1, \dots, r, \theta, \omega, \mathbf{s}_{1x}, \dots, \mathbf{s}_{1y}, \dots, \mathbf{s}_{1z}, \dots) - W] \times \\ \times \psi_{s_1, \dots, s_f}(x_1, \dots, y_1, \dots, z_1, \dots, r, \theta, \omega) = 0 \quad (5)$$

where $\mathbf{s}_{kx}, \mathbf{s}_{ky}, \mathbf{s}_{kz}$ are the *Pauli* spin operator components for the k th electron contained in the expression of the potential energy. As applied to the eigenfunction ψ , the above operators have the following properties:

$$\begin{aligned} \mathbf{s}_{kx}\psi_{a_1, \dots, a_k, \dots} &= \frac{1}{2}\hbar\psi_{a_1, \dots, b_k, \dots}; & \mathbf{s}_{kx}\psi_{a_1, \dots, b_k, \dots} &= \frac{1}{2}\hbar\psi_{a_1, \dots, a_k, \dots} \\ \mathbf{s}_{ky}\psi_{a_1, \dots, a_k, \dots} &= -\frac{1}{2}i\hbar\psi_{a_1, \dots, b_k, \dots}; & \mathbf{s}_{ky}\psi_{a_1, \dots, b_k, \dots} &= \frac{1}{2}i\hbar\psi_{a_1, \dots, a_k, \dots} \\ \mathbf{s}_{kz}\psi_{a_1, \dots, a_k, \dots} &= \frac{1}{2}\hbar\psi_{a_1, \dots, a_k, \dots}; & \mathbf{s}_{kz}\psi_{a_1, \dots, b_k, \dots} &= -\frac{1}{2}\hbar\psi_{a_1, \dots, b_k, \dots} \end{aligned} \quad (6)$$

for brevity the positional coordinates being omitted from the eigenfunctions.

Written out in detail, (5) becomes

$$\left[\mathbf{H}_0 - \frac{\hbar^2}{8\pi^2\mu r^2} \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \cot \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} + \operatorname{cosec}^2 \theta \frac{\partial^2}{\partial \omega^2} \right) - W \right] \times \\ \times \psi_{s_1, \dots, s_f}(x_1, \dots, y_1, \dots, z_1, \dots, r, \theta, \omega) = 0 \quad (7)$$

where $\mu = \frac{M_1 M_2}{M_1 + M_2}$ is the *reduced mass* of the molecule, and

$$\mathbf{H}_0 = -\frac{\hbar^2}{2m} \sum_i \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) + V_{\text{nuc}}(r) + V_{\text{el, nuc}}(x_i, y_i, z_i, r) + \mathbf{H}^s(s_i) \quad (8)$$

The first term of (8) is the kinetic energy operator of the electrons; $V_{\text{nuc}}(r) = Z_1 Z_2 e^2 / r$ is the mutual potential energy of the nuclei; $V_{\text{el, nuc}}(x_i, y_i, z_i, r)$ is the *Coulomb* potential of the electrons with respect to the nuclei and to each other; $\mathbf{H}^s(s_i)$ represents the spin interaction terms. All terms are expressed in the space-fixed coordinate system.

Since in case *a* the influence of the electron spin upon the molecular motion is strong, it is advisable to examine the entire wave equation in a coordinate system moving together with the molecule. Upon introducing these coordinates from (2), the wave equation (5) becomes

$$[\mathbf{H}(\xi_1, \dots, \eta_1, \dots, \zeta_1, \dots, r, \theta, \omega, s_{1x}, \dots, s_{1y}, \dots, s_{1z}, \dots) - W] \times \\ \times (\psi_{s_1, \dots, s_f}(\xi_1, \dots, \eta_1, \dots, \zeta_1, \dots, r, \theta, \omega) = 0 \quad (9)$$

In this form of the wave equation, however, the spins still refer to the space-fixed coordinate system. In order to transform these into a molecule-fixed system, $s_{1\xi}, \dots, s_{1\eta}, \dots, s_{1\zeta}, \dots$ (for which relationships like (6) are valid) should first be substituted for $s_{1x}, \dots, s_{1y}, \dots, s_{1z}, \dots$ in the expression of \mathbf{H} ; next, the eigenfunction $\psi_{s_1, \dots, s_f}(\quad)$ should also be transformed into the new system as follows:

$$\psi_{s_1, \dots, s_f} = \sum_{\sigma_1, \dots, \sigma_f} S(s_1, \dots, s_f; \sigma_1, \dots, \sigma_f) \psi_{\sigma_1, \dots, \sigma_f} \quad (10)$$

where the transformation matrix \mathbf{S} can, after Neumann and Wigner [162], be written in terms of the transformation matrix elements of the individual electrons in the form

$$S(s_1, \dots, s_f; \sigma_1, \dots, \sigma_f) = S(s_1; \sigma_1) \dots S(s_f; \sigma_f) \quad (11)$$

where, according to Pauli [174]:

$$S(a_k; \alpha_k) = \cos \frac{\theta}{2} e^{-\frac{i}{2}(\omega + \frac{\pi}{2})}; \quad S(a_k; \beta_k) = -i \sin \frac{\theta}{2} e^{-\frac{i}{2}(\omega + \frac{\pi}{2})} \\ S(b_k; \alpha_k) = -i \sin \frac{\theta}{2} e^{\frac{i}{2}(\omega + \frac{\pi}{2})}; \quad S(b_k; \beta_k) = \cos \frac{\theta}{2} e^{\frac{i}{2}(\omega + \frac{\pi}{2})} \quad (12)$$

Upon substituting the form (10) of the eigenfunction into (9) and multiplying (9) from the left by the reciprocal of the matrix (11), we obtain

$$[\mathbf{S}^{-1} \mathbf{H}(\xi_1, \dots, \eta_1, \dots, \zeta_1, \dots, r, \theta, \omega, s_{1\xi}, \dots, s_{1\eta}, \dots, s_{1\zeta}, \dots) \mathbf{S} - W] \times \\ \times \psi_{\sigma_1, \dots, \sigma_f}(\xi_1, \dots, \eta_1, \dots, \zeta_1, \dots, r, \theta, \omega) = 0 \quad (13)$$

In the course of the detailed development of these steps let us first examine (8). After the transformation, this expression will have the form

$$\mathbf{H}'_a = \mathbf{S}^{-1} \mathbf{H}_0 \mathbf{S} = -\frac{\hbar^2}{2m} \sum_i \left(\frac{\partial^2}{\partial \xi_i^2} + \frac{\partial^2}{\partial \eta_i^2} + \frac{\partial^2}{\partial \zeta_i^2} \right) \\ + V_{\text{nuc}}(r) + V_{\text{el, nuc}}(\xi_i, \eta_i, \zeta_i, r) + \mathbf{H}_a^s(\sigma_i) \quad (14)$$

where the first term on the right-hand side is the kinetic energy operator of the electrons of a molecule with *fixed nuclei*; the second and third terms

are the potential energy expressions for the nuclei and the electrons, respectively; $\mathbf{H}_a^s(\sigma_i) = \mathbf{S}^{-1} \mathbf{H}^s(s_i) \mathbf{S}$ is a spin interaction term expressed in the molecule-fixed system.

In the second part of (7), in the differentiations with respect to θ and ω it should be taken into account that, apart from the direct dependence upon the coordinates, the system ξ, η, ζ also depends by (3) on θ and ω , and so does S by (11) and (12). Thus, distinguishing this total differentiation by a suffix s from the differentiation in the molecule-fixed system, we get e.g.

$$\mathbf{S}^{-1} \frac{\partial}{\partial \omega_s} \mathbf{S} = \frac{\partial}{\partial \omega} + \sum_{k=1}^f \left(\frac{\partial}{\partial \xi_k} \frac{\partial \xi_k}{\partial \omega} + \frac{\partial}{\partial \eta_k} \frac{\partial \eta_k}{\partial \omega} + \frac{\partial}{\partial \zeta_k} \frac{\partial \zeta_k}{\partial \omega} - i \mathbf{s}_{kz} \right) \quad (15)$$

Now since by (2) and (3)

$$\frac{\partial \xi_k}{\partial \omega} = \eta_k \cos \theta - \zeta_k \sin \theta, \quad \frac{\partial \eta_k}{\partial \omega} = -\xi_k \cos \theta, \quad \frac{\partial \zeta_k}{\partial \omega} = \xi_k \sin \theta \quad (16)$$

and furthermore, by (2),

$$\mathbf{s}_{kz} = \mathbf{s}_{k\eta} \sin \theta + \mathbf{s}_{k\zeta} \cos \theta \quad (17)$$

Eqn. (15) can be written as

$$\mathbf{S}^{-1} \frac{\partial}{\partial \omega_s} \mathbf{S} = \frac{\partial}{\partial \omega} - i(\mathbf{P}_\zeta \cos \theta + \mathbf{P}_\eta \sin \theta) \quad (18)$$

where

$$\mathbf{P}_\zeta = \sum_{k=1}^f \left[-i \left(\xi_k \frac{\partial}{\partial \eta_k} - \eta_k \frac{\partial}{\partial \xi_k} \right) + \mathbf{s}_{k\zeta} \right] = \sum_{k=1}^f (\mathbf{L}_{k\zeta} + \mathbf{s}_{k\zeta}) = \mathbf{L}_\zeta + \mathbf{S}_\zeta \quad (19)$$

and similar expressions hold for the other components. The operator (19) corresponds to the ζ component of the resultant angular momentum of the electrons, i.e. the ζ component of the resultant of the orbital angular momenta and the spin momenta, expressed in the molecule-fixed system.

It can similarly be shown that

$$\mathbf{S}^{-1} \frac{\partial}{\partial \theta_s} \mathbf{S} = \frac{\partial}{\partial \theta} - i \mathbf{P}_\xi \quad (20)$$

By the above relationships, in case *a* Eqn. (7) has the form

$$\left\{ \mathbf{H}'_a - \frac{h^2}{8\pi^2 \mu r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \cot \theta \left(\frac{\partial}{\partial \theta} - i \mathbf{P}_\xi \right) + \left(\frac{\partial}{\partial \theta} - i \mathbf{P}_\xi \right)^2 \right. \right. \\ \left. \left. + \operatorname{cosec}^2 \theta \left(\frac{\partial}{\partial \omega} - i \mathbf{P}_\zeta \cos \theta - i \mathbf{P}_\eta \sin \theta \right)^2 \right] - W \right\} \times \\ \times \psi_{\sigma_1, \dots, \sigma_f}(\xi_1, \dots, \eta_1, \dots, \zeta_1, \dots, r, \theta, \omega) = 0 \quad (21)$$

In the case of a weak spin interaction (i.e. in case *b*), a similar procedure will be applied, with the difference that, since in this case the spins will be referred to a space-fixed system, the transformation (10) is not necessary. In this case, the following result is obtained:

$$\begin{aligned} & \left\{ \mathbf{H}'_b - \frac{\hbar^2}{8\pi^2\mu r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \cot \theta \left(\frac{\partial}{\partial \theta} - i\mathbf{L}_\xi \right) + \left(\frac{\partial}{\partial \theta} - i\mathbf{L}_\xi \right)^2 \right. \right. \\ & \quad \left. \left. + \operatorname{cosec}^2 \theta \left(\frac{\partial}{\partial \omega} - i\mathbf{L}_\xi \cos \theta - i\mathbf{L}_\eta \sin \theta \right)^2 \right] - W \right\} \times \\ & \quad \times \psi_{s_1, \dots, s_f}(\xi_1, \dots, \eta_1, \dots, \zeta_1, \dots, r, \theta, \omega) = 0 \end{aligned} \quad (22)$$

where \mathbf{H}'_b is of the same form as \mathbf{H}'_a in (14), except that in this case $\mathbf{H}^s(s_i)$ stands instead of $\mathbf{S}^{-1} \mathbf{H}^s(s_i) \mathbf{S}$; for the sake of uniform notation, $\mathbf{H}^s_b(s_i)$ will denote $\mathbf{H}^s(s_i)$.

If certain members, to be dealt with in detail later, are omitted from (21), then (21) is solved by an eigenfunction of the following form:

$$\begin{aligned} & \psi_{\sigma_1, \dots, \sigma_f}(\xi_1, \dots, \eta_1, \dots, \zeta_1, \dots, r, \theta, \omega) \\ & = \Phi_{n, \Lambda, \Sigma}(\xi_i, \eta_i, \zeta_i, \sigma_i, r) R_{n, v}(r) u_{J, \Omega, M}(\theta, \omega) \end{aligned} \quad (23)$$

Substituting this into (21), we get

$$[\mathbf{H}'_a - W_0(r)] \Phi_{n, \Lambda, \Sigma}(\xi_i, \eta_i, \zeta_i, \sigma_i, r) = 0 \quad (24a)$$

$$\left[\frac{\hbar^2}{8\pi^2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - W_0(r) - W_{\text{rot}}(r) - \bar{U}(r) + W \right] R_{n, v}(r) = 0 \quad (24b)$$

$$\begin{aligned} & \left\{ \frac{\hbar^2}{8\pi^2\mu r^2} \left[\cot \theta \frac{\partial}{\partial \theta} + \frac{\partial^2}{\partial \theta^2} + \operatorname{cosec}^2 \theta \left(\frac{\partial}{\partial \omega} - i\Omega \cos \theta \right)^2 \right] + \right. \\ & \quad \left. + W_{\text{rot}}(r) \right\} u_{J, \Omega, M}(\theta, \omega) = 0 \end{aligned} \quad (24c)$$

In (24a), $W_0(r)$ is the eigenvalue of the molecule with fixed nuclei, in the state described by the eigenfunction $\Phi_{n, \Lambda, \Sigma}$; it contains the internuclear distance as a parameter.

The eigenfunction $\Phi_{n, \Lambda, \Sigma}$ depends (apart from the internuclear distance) solely on the positional and spin coordinates of the electrons; therefore it is usually called the *electronic part* of the eigenfunction. Here Λ and Σ are the quantum numbers of the components parallel to the internuclear axis of the resultant orbital angular momentum and spin momentum of the electrons, and n denotes the rest of the quantum numbers of the electrons. If, in the first approximation, the interaction between the orbital angular

momenta and the spins of the electrons is neglected, $\Phi_{n,\Lambda,\Sigma}$ can be written in the form

$$\bar{\Phi}_{n,\Lambda}(\xi_i, \eta_i, \zeta_i, r) \chi_{\Sigma}(\sigma_i) \quad (25)$$

where the first factor of the product is the eigenfunction of the electrons without the spin, which is therefore the function of the positional coordinates only, the second factor is the spin eigenfunction. Since Λ , Σ and the resultant spin momentum S of the electrons are well-defined quantum numbers in this approximation, the eigenfunctions $\Phi_{n,\Lambda,\Sigma}$ are not only the solutions of (24a) but also the simultaneous eigenfunctions of the operators $\mathbf{L}_{\zeta} = \sum_i \mathbf{l}_{\zeta i}$, $\mathbf{S}_{\zeta} = \sum_i \mathbf{s}_{\zeta i}$ and $\mathbf{S}^2 = \mathbf{S}_{\xi}^2 + \mathbf{S}_{\eta}^2 + \mathbf{S}_{\zeta}^2$. These requirements can be satisfied by the linear combinations derived from (25), taking into consideration that according to the *Pauli* principle, the eigenfunctions must be anti-symmetric with respect to the exchange of any two electrons. Hence,

$$\Phi_{n,\Lambda,\Sigma} = \sum_{\Lambda} \sum_{\Sigma} \bar{\Phi}_{n,\Lambda}(\xi_i, \eta_i, \zeta_i, r) \chi_{\Sigma}^{\Lambda}(\sigma_i) \quad (26)$$

where the summation must be extended over all possible compositions of the quantities $\Lambda = \sum_i c_i \lambda_i$ and $\Sigma = \sum_i c'_i \sigma_i$. In these cases c_i and $c'_i = \pm 1$ according as the component of the orbital angular momentum of the individual electrons is parallel or antiparallel to the internuclear axis.

In (24b) and (24c), $W_{\text{rot}}(r)$ is the eigenvalue of (24c), as will be shown in detail below. For (24c), the relation $\mathbf{P}_{\zeta} \Phi = \Omega \Phi$ is taken, where $\Omega = \Lambda + \Sigma$ is the sum of the components parallel to the inter-nuclear axis of the resultant orbital and resultant spin angular momenta of the electrons in a molecule with fixed nuclei; Ω is either an integer or a half integer according as the number of the electrons is even or odd.

Finally, $\bar{U}(r)$ in (24b) is the average, over the electron coordinates, of the terms neglected on separation, and W is the total energy of the molecule. This chapter will be devoted also to the calculation of this latter.

Before entering upon these discussions, let us first write up the terms neglected on separation. These are

$$\begin{aligned} \mathbf{H}_{1a}^p = \frac{\hbar^2 i}{8\pi^2 \mu r^2} \left[\mathbf{P}_{\xi} \left(2 \frac{\partial}{\partial \theta} + \cot \theta \right) + 2 \operatorname{cosec} \theta \mathbf{P}_{\eta} \frac{\partial}{\partial \omega} \right. \\ \left. - i \cot \theta (\mathbf{P}_{\eta} \mathbf{P}_{\zeta} + \mathbf{P}_{\zeta} \mathbf{P}_{\eta}) \right] \end{aligned} \quad (27a)$$

and

$$\mathbf{H}_{2a}^p = \frac{\hbar^2}{8\pi^2 \mu r^2} \left[(\mathbf{P}_{\xi}^2 + \mathbf{P}_{\eta}^2) - \frac{r^2}{\Phi} \frac{\partial^2 \Phi}{\partial r^2} - \frac{2r^2}{\Phi R} \frac{\partial \Phi}{\partial r} \frac{\partial R}{\partial r} - \frac{2r}{\Phi} \frac{\partial \Phi}{\partial r} \right] \quad (27b)$$

This latter disappears on averaging over the electron coordinates. It is to be noted that the part which does not disappear over such an averaging as $\bar{U}(r) = \int \Phi_n^* \mathbf{H}_{2a}^p \Phi_n d\tau$ is contained in (24b). These expressions will be discussed at greater length in Section 1.3.

In order to calculate W , the total energy of the molecule, (24b) has to be solved. For this purpose, the forms of $W_{\text{rot}}(r)$ and $W_0(r)$ have to be known. These are, however, the solutions of (24c) and (24a), respectively. Let us deal first with the latter.

Equation (24c), as is known in quantum mechanics, is the wave equation of the *symmetric top*, whose solution has been discussed by Reiche and Rademacher [189, 184], by Kronig and Rabi [137], and by Dennison [40]. For the eigenvalue of the equation, these authors have obtained the expression

$$W_{\text{rot}}(r) = \bar{B}[J(J+1) - \Omega^2]; \quad \bar{B} = \frac{h^2}{8\pi^2\mu r^2} \quad (28)$$

where J is the *rotational quantum number*, which can assume the values $|\Omega|, |\Omega+1|, \dots$. The form of the eigenfunction is

$$u_{J,\Omega,M}(\theta, \omega) = N x^{s/2} (1-x)^{d/2} F(1+d+s+p, -p, 1+s, x) e^{iM\omega} \quad (29)$$

where

$$x = 1/2(1 + \cos \theta); \quad s = |M + \Omega|; \quad d = |M - \Omega|; \quad p = J - 1/2(d + s)$$

$$M = -J, -J+1, \dots, +J$$

and

$$N = \left[\frac{(-1)^d (s+p)! (d+s+p)! (1+d+s+2p)!}{4\pi p! (d+p)! (s!)^2} \right]^{1/2} \quad (30)$$

the hypergeometric function F is of the form

$$F(1+d+s+p, -p, 1+s, x) = \frac{x^{-s}(1-x)^{-d}s!}{(s+p)!} \times \frac{d^p}{dx^p} [x^{p+s}(1-x)^{p+d}] \quad (31)$$

Equation (24a) is the wave equation of the molecule with fixed nuclei (the *stationary molecule*). The exact solution of this equation is difficult from the mathematical point of view when many electrons are involved, but the use of simplifying assumptions helps in obtaining approximate eigenfunctions. The explicit form of the eigenvalues, naturally containing r as parameter, could be derived only for two electrons [72, 94], and then only for the ground state. This formula is, however, so complicated that it is applicable only in numerical computations. Still, (24a) plays an important role in describing the behaviour of the rotational terms, and for this reason it will be dealt with in detail in Section 1.2.

Expressions for the energy levels of the molecule can be obtained from (24b). To solve this equation, the knowledge of $W_{\text{rot}}(r)$ is not enough; it is necessary to know $W_0(r)$ or, at least its dependence on r . Since (24a) cannot be solved in general, it is usual to make some approximative assumption as

to the dependence of $W_0(r)$ on r . This then leads to expressions that provide a good fit to the empirically determined potential curve and, in addition, enable to obtain simple solutions for (24b). Such approximations were reported by Kratzer [133], Rosen and Morse [190], Pöschl and Teller [177],

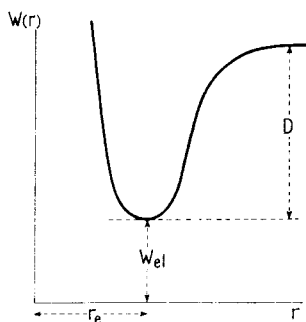


Fig. 1.2 The schematic Morse potential function.

Hylleraas [85], Morse [151] and many others (see e.g. Varshni [209]). In the present treatment the approximation given by Morse [151] will be used, as it preserves best the *anharmonic oscillator* character of (24b). The analytical expression of the Morse approximation (see Fig. 1.2) is

$$W_0(r) = W_{el} + D[1 - e^{-a(r-r_e)}]^2 \quad (32)$$

where W_{el} is the value of the potential curve at equilibrium internuclear distance (r_e), D is the dissociation energy as referred to this equilibrium; and a is a constant characteristic of the electronic state in question. Substituting (28) and (32) into (24b) and determining the eigenvalue of W will now yield the total energy

of the molecule. The goal of this chapter is to determine this quantity.

In order to solve (24b), let us put $P = R/r$, $W' = W - W_{el} - D$ and neglect $\bar{U}(r)$. Multiplying by $8\pi^2\mu/\hbar^2$ and introducing the new variable $y = e^{-a(r-r_e)}$ [151, 175], we obtain

$$\frac{d^2P}{dy^2} + \frac{1}{y} \frac{dP}{dy} + \frac{8\pi^2\mu}{a^2\hbar^2} \left(\frac{W'}{y^2} + \frac{2D}{y} - D - \frac{Ar_e^2}{y^2r^2} \right) P = 0 \quad (33)$$

where

$$A = \frac{\hbar^2}{8\pi^2\mu r_e^2} [J(J+1) - \Omega^2] \quad (34)$$

Since $y = e^{-a(r-r_e)}$ implies $\log y = -a(r-r_e)$, we get, developing into a power series about $y = 1$ (i.e. about $r = r_e$) and neglecting higher-order terms, the expression

$$\frac{r_e^2}{r^2} = \frac{1}{\left(1 - \frac{\log y}{r_e a}\right)^2} = 1 + \frac{2}{ar_e}(y-1) + \left[-\frac{1}{ar_e} + \frac{3}{a^2 r_e^2}\right](y-1)^2 + \dots \quad (35)$$

It can be shown [172] that the terms neglected on the expansion do not essentially influence the final result. Replacing $(r_e/r)^2$ in (33) by (35) one arrives at

$$\frac{d^2P}{dy^2} + \frac{1}{y} \frac{dP}{dy} + \frac{8\pi^2\mu}{a^2\hbar^2} \left[\frac{W' - c_0}{y^2} + \frac{2D - c_1}{y} - D - c_2 \right] P = 0 \quad (36)$$

where

$$c_0 = A \left[1 - \frac{3}{ar_e} + \frac{3}{a^2 r_e^2} \right]; c_1 = A \left[\frac{4}{ar_e} - \frac{6}{a^2 r_e^2} \right]; c_2 = A \left[-\frac{1}{ar_e} + \frac{3}{a^2 r_e^2} \right] \quad (37)$$

Since the only independent variable in (36) is y , let $y = z/2d$ and $P(y) = Ne^{-z/2} z^{b/2} E(z)$, where N is a normalizing factor, and

$$d^2 = \frac{8\pi^2\mu(D + c_2)}{a^2\hbar^2}; \quad b^2 = -\frac{32\pi^2\mu(W' - c_0)}{a^2\hbar^2} \quad (38)$$

The final form of the equation then becomes

$$\frac{d^2 E}{dz^2} + \frac{b - z + 1}{z} \frac{dE}{dz} + \frac{v}{z} E = 0 \quad (39)$$

where

$$v = \frac{4\pi^2\mu(2D - c_1)}{a^2\hbar^2 d} - \frac{b + 1}{2} \quad (40)$$

If the condition is such that v can assume only integer values, then $E(z)$ in (39) will be a generalized *Laguerre* polynomial; by substituting b and d from (38) into the expression of v in (40), and by substituting c_0, c_1, c_2 from (37), it is possible to express W' , or W itself. Division by $\hbar c$ of the expression for W leads to

$$F = F_{el} + \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + B_v[J(J + 1) - \Omega^2] - D_v[J(J + 1) - \Omega^2]^2 \quad (41)$$

where v is the *vibrational quantum number* and

$$F_{el} = \frac{W_{el}}{\hbar c}; \quad \omega_e = \frac{a}{c\pi} \sqrt{\frac{D}{2\mu}}; \quad x_e = \frac{\hbar c \omega_e}{4D} \\ B_v = B_e - \alpha_e(v + 1/2); \quad D_v = D_e \quad (42)$$

$$B_e = \frac{\hbar}{8\pi^2\mu c r_e^2}; \quad \alpha_e = 2B_e x_e \left[3 \sqrt{\frac{B_e}{\omega_e x_e}} - 3 \frac{B_e}{\omega_e x_e} \right]; \quad D_e = \frac{4B_e^3}{\omega_e^2}$$

The expression (41) compares most favourable with the empirical formula (2) given in the Introduction.

The structure of the empirical formula (2) is now clear, as well as the origin of its denotation. In the first term of (41), W_{el} corresponds—by (32)—to the minimum of the potential curve in Fig. 1.2, and since this value depends on the electron configuration only, it is called *electron energy*.

In the second term of (41), ω_e is the difference between the vibrational levels of the harmonic oscillator, and $\omega_e x_e$ in the third term is the deviation from the above value, i.e. the degree of anharmonicity in the real molecule; consequently, these two terms give together the energy of the *anharmonic oscillator*. The next to the last term is the energy of the *symmetric top*, which

accounts also for the change of the inter-nuclear distance in the higher vibrational state, and the last term is the *centrifugal correction*, arising from the increase in the inter-nuclear distance during higher-energy rotation; it will be dealt with in detail in Section 1.4.

It is seen that the exact wave-mechanical treatment convincingly confirms the results obtained from the model, but it also points out the limitations of the latter. The model gives correct results in all those cases when the separation of the wave equation can be effected, or, more precisely, when the terms omitted on separation are really negligible.

The solution of (24b) not only makes possible the formal proof of the empirical formula (2) and the mechanical interpretation of its terms but also quantitative relationships among the empirical coefficients and molecular constants already known. Thus, following the empirical determination of the dissociation energy D , and of the constants B_e , α_e , D_e , ω_e , $\omega_e x_e$, the validity of (42) can be checked; in doing so we may check also the adequacy of the theory. Experience shows that the theoretical expressions in (42) yield good approximations to reality for many diatomic molecules (Pekeris [175]).

The procedure described above can be applied also to case *b*, i.e. to the solution of (22). All the difference is that in the term formula (41) and everywhere else A is used instead of Ω (where A is the component of the resultant orbital angular momentum of the electrons parallel to the inter-nuclear axis; it can assume only integer values), and in (27a) and (27b) the components of the operator \mathbf{L} will occur instead of those of the operator \mathbf{P} .

Between two positively charged nuclei there is a strong electric field possessing a rotational symmetry round the internuclear axis, therefore, in both cases *a* and *b* only A , the parallel component of the resultant orbital angular momentum of the electrons, can be defined; \vec{L} , the orbital angular momentum cannot be defined. Thus the *electron states* of the molecule are defined by the quantum number A , as against \vec{L} for the atoms. To quantum numbers A of different magnitudes, there correspond *in general* electron states (or terms) of totally different electron configurations, far apart energetically. The symbols used here follow those used for atoms; for $A = 0, 1, 2 \dots$ the symbols of the molecular terms are $\Sigma, \Pi, \Delta \dots$

The negative values of A need not be dealt with separately, as e.g. the two electron states belonging to $A = +1$ and $A = -1$ differ only in the sense of rotation of the electrons around the inter-nuclear axis, so that the energies of the two states are equal. In the quantum-mechanical treatment this is expressed by saying that the states belonging to the positive and negative values of A are degenerate and that the corresponding eigenfunctions are linear combinations of opposite symmetry of the eigenfunctions belonging to the positive and negative values of A :

$$\begin{aligned}\psi_A^+ &= \frac{1}{\sqrt{2}} [\psi_{+A} + \psi_{-A}] \\ \psi_A^- &= \frac{1}{\sqrt{2}} [\psi_{+A} - \psi_{-A}]\end{aligned}\tag{43}$$

Under increasing rotation, however, the terms (27) expressing the coupling of the electronic motion to the rotation of the nuclei—which have been neglected in our first-approximation solution of the wave equation—result by the theory of perturbation in a splitting of this twofold degenerate state. This phenomenon is called *A-type doubling* or *splitting*. The detailed treatment of this problem will be given in Chapter 2.

It should be noted here that the individual states can also be classified according to the behavior of the electronic and rotational parts of the eigenfunctions under certain symmetry operations. The reader is referred for detailed information e.g. to Herzberg [4]. In the present study, wherever required only essential detail will be given (see Section 4.1).

1.2. INTERACTIONS OF THE ELECTRON SPIN

The results discussed so far suffice to integrate only a part of the observed molecular spectra. It has frequently been observed that in certain band systems all bands are of doublet structure; in others they are of triplet or even multiplet structure, meaning that each line within the band is, in fact, composed of two (or three or more) closely spaced lines. It is logical to refer this *multiplet structure* of the bands to the *electron spin*, as is done in the case of multiplet splitting in atomic spectra.

The spins of the individual electrons form a resultant spin vector \vec{S} , whose magnitude is defined by the spin quantum number S . (The magnitude of \vec{S} is $\sqrt{S(S+1)}\hbar$.) S is either a half-integer or an integer, according as the total number of electrons in the molecule is odd or even.

The motion of the electrons and nuclei in the molecule, the resultant spin and even the spins of the individual electrons are not wholly independent of one another; certain interactions exist among them. This becomes fairly obvious if one stops to think that the motions of the electrons and of the nuclei are in effect electric currents producing magnetic fields, further, that an intrinsic basic property of the spin is its magnetic momentum. There is an interaction between the magnetic fields of the moving electrons and nuclei on the one hand, and the resultant spin (and also the spins of the individual electrons) on the other hand.

In case *a*, when the molecule is best examined in the molecule-fixed system, the interaction between the spin and the parallel component of the resultant orbital angular momentum of the electrons makes the resultant spin vector \vec{S} precess around the inter-nuclear axis in such a manner that its parallel component is $\Sigma\hbar$ (Fig. 1.3), where Σ is the quantum number (in the present case, Σ does not refer to the electron state $\Lambda=0$!). Σ can assume any one of the $2S+1$ values: $S, S-1, \dots, -S+1, -S$.

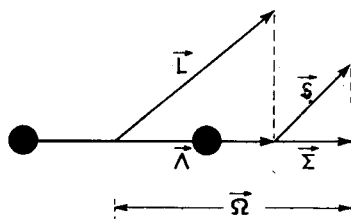


Fig. 1.3 Connection between spin vector and molecular axis in a molecule at rest.

To an electronic state of a given Λ there belong, then, $2S + 1$ substates—according to the possible orientations of the \vec{S} spin—whose energy levels are evenly spaced to a good approximation (the energy difference between any two neighbouring substates is the same). This is why the number $2S + 1$ is called the *multiplicity* of the electron state in question; it is used as left-hand superfix of the term symbol. For example, the symbols $^1\Sigma$, $^2\Pi$, $^3\Delta$ etc. denote, in this order, the singlet Σ , doublet Π , triplet Δ etc. terms. Each substate could be characterized by the appropriate value of the quantum number Σ ; instead, the sum $\Omega = \Lambda + \Sigma$ is normally used, however. It is given as a right-hand suffix. Thus, for example, a $^2\Pi$ term ($\Lambda = 1$) has two substates or components; one of these (with $\Sigma = -1/2$) is denoted $^2\Pi_{1/2}$; the other is denoted $^2\Pi_{3/2}$. In the case of a $^3\Pi$ term, the components are $^3\Pi_0$, $^3\Pi_1$, $^3\Pi_2$.

The magnitude of multiplet splitting, i.e. the energy differences between the individual term components, can be rather different for the electron terms Π , Δ , . . . , of the molecules; however, for any Σ term, the multiplet splitting is zero in a first approximation, i.e. the term components nearly coincide, since in the case of the Σ terms the parallel component of the resultant orbital angular momentum of the electrons $\Lambda = 0$, with the result that there is no interaction between the motion of the electrons and the spin. The spin can still be oriented in $2S + 1$ ways, but there is no reason for any energy difference to exist between these orientations.

Experience shows, however, a slight splitting here also. The explanation is that, in addition to the interaction mentioned above, there is a weaker *spin-spin interaction* among the spins of the individual electrons which produces energy differences between levels of different $|\Sigma|$. This interaction obviously occurs also when $\Lambda \neq 0$, but then it is overshadowed by the much stronger *spin-orbit interaction*. For the Σ term, however, the spin-orbit interaction is zero and it is the spin-spin interaction that produces a slight but observable splitting. There is also an even weaker interaction, due to rotation; for that see later.

The rotation of the molecule affects the interactions. Hund [84] was the first to examine this phenomenon, and he did so even before the advent of the wave-mechanical conception. The essence of Hund's idea was to distinguish one by one the typical interactions among the numerous that occur in the molecule and to define in this way various limiting-case models which he called cases *a*, *b*, *c*, *d* and *e*. In the present discussion we shall restrict our attention to Hund's cases *a*, *b* and *d* and give brief, model-like description of those; in the following chapter, their details will be developed on a wave-mechanical basis.

In Hund's case *a*, rotation is assumed to have little influence upon the conditions existing in the fixed molecule. In other words, the spin is so strongly coupled to the inter-nuclear axis that its parallel component remains quantized even in the rotating molecule, so that Σ remains a well defined quantum number (and hence $\Omega = \Lambda + \Sigma$ also remains well defined). The molecule therefore behaves as a symmetric top whose angular momentum with respect to the inter-nuclear axis is defined by Ω , while its total angular momentum is given by the quantum number J ; J can assume the values

$|\Omega|, |\Omega| + 1, \dots$ (Fig. 1.4). In this case, which is identical with case *a* described in the previous section, a separable wave equation can be derived. When the interaction between spin and rotation is examined, the terms (1.1-27a) and (1.1-27b) omitted on the separation of the wave equation, can be taken into account by means of a perturbation calculation. This interaction affects the multiplet splitting, indeed, no results in agreement with experiments can be obtained without taking it into account. Moreover, the rotation essentially influences also the spin-orbit and spin-spin interactions.

In *Hund's case b* the spin is not coupled (or is very weakly coupled) to the inter-nuclear axis. By our previous statement, all Σ terms are of such nature. The molecule rotates, in fact, as if there existed no spin: the resultant \vec{N} is composed of \vec{A} and the (unquantized) angular momentum \vec{R} of the rotation of the nuclei (Fig. 1.5). The magnitude of \vec{N} is defined by the quantum number N ; $N = |A|, |A| + 1, \dots$; therefore \vec{N} plays the same role here as \vec{J} does in the singlet states. This model corresponds to the case described by the separated wave equation (case *b* in the previous section). The rotation of the molecule gives rise to a magnetic field (due to the movement of the charges), having the same orientation as \vec{N} . In the case of a strong rotation this magnetic field will become so strong that, compared with this interaction, the \vec{S} spin will be only weakly coupled to the inter-nuclear axis and may be regarded as practically free. It will consequently combine with \vec{N} to give the total angular momentum of the rotating molecule. The symbol for total angular momentum is, as usual, \vec{J} . The quantum number J , determining the magnitude of \vec{J} , can assume values as $N + S, N + S - 1, \dots, |N - S|$. In this case, too, for a given \vec{N} , \vec{S} can be oriented in $2S + 1$ ways (provided, as is usual, that $N \geq S$). Hence, each N level is split into $2S + 1$ sublevels, but the energy difference between these is zero in the ideal case *b*. In fact there is in most cases some slight splitting owing to the modified form, valid in case *b*, of the spin-orbit and spin-spin interactions. These splittings are taken

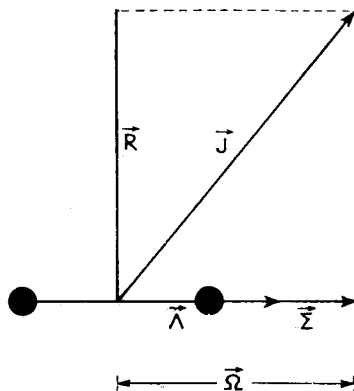


Fig. 1.4 Vector model of *Hund's case a*.

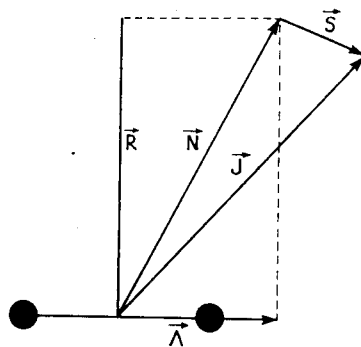


Fig. 1.5 Vector model of *Hund's case b*.

into account in a rigorous discussion. As this section is about spin interactions, and as in *Hund's case d* the dominant feature is the interaction between rotation and orbital angular momentum, the more detailed discussion of this case will be referred to the next section. Let us here note only that this latter type of interaction also appears in both cases *a* and *b* and leads to the splitting of the twofold degenerate levels deriving from the positive and negative orientation of Λ (which would coincide otherwise). This type of splitting was formerly called *Λ -type doubling*. Accordingly, *Λ -type splitting* is the beginning of the transition toward *Hund's case d*. Quantum-mechanically it can be treated by taking into account the terms neglected on the separation of the wave equation in both cases *a* and *b*.

For a rigorous wave-mechanical study of spin interactions, the electronic part of the wave equation discussed in Section 1.1 is to be analysed in detail. Let us do this separately for cases *a* and *b*.

Case a. First let us find the terms making up the operator \mathbf{H}'_a in (1.1-24a). The *Breit* wave equation for atoms containing two electrons has in the *Pauli* approximation and in the absence of external fields, six well-separable groups of terms [1]. The electron spin occurs only in two groups. One of these describes the *spin-orbit* interaction, i.e. the interaction between the magnetic momentum assigned to the orbital angular momentum of the electrons and the spin magnetic moments; the other corresponds to the interaction between the magnetic dipole moments of the two electron spins, i.e. to the *spin-spin* interaction. In the discussion of the interactions of electron spins in molecules with more than two electrons, it seems advisable to adopt similar terms and to complement the formula with a term—to be derived in detail later—which is due to the rotation of the molecule, and which therefore has no equivalent in atoms. Accordingly, the last term of (1.1-14) in the molecule-fixed system will be

$$\mathbf{H}_a^s(\sigma_i) = \mathbf{H}_a^{so} + \mathbf{H}_a^{ss} + \mathbf{H}_a^{sr} \quad (1)$$

where the first term on the right-hand side is the spin-orbit interaction, and the second and third terms describe the spin-spin and *spin-rotation* interactions, respectively. Let us examine these separately.

(a) *Spin-Orbit Interaction.* Following Heisenberg [70], the term describing the interactions between the spin of an electron and its own orbit, on the one hand, and the spin of an electron and the orbit of another electron, on the other, can be written as

$$\mathbf{H}_a^{so} = \frac{\hbar c^2}{4\pi m c^2} \sum_k \left\{ \left[\frac{Z_a}{r_{ka}^3} (\mathbf{r}_{ka} \times \mathbf{v}_k) + \frac{Z_b}{r_{kb}^3} (\mathbf{r}_{kb} \times \mathbf{v}_k) - \sum_{k' > k} \frac{1}{r_{kk'}^3} (\mathbf{r}_{kk'} \times (\mathbf{v}_k - 2\mathbf{v}_{k'})) \right] \mathbf{s}_k \right\} \quad (2)$$

where \mathbf{r}_{ka} (\mathbf{r}_{kb}) are the operators of the distance between the k th electron and the nucleus a (b); $\mathbf{r}_{kk'}$ is the distance between the k th and the k' th electrons, Z_a and Z_b are the respective nuclear charges, \mathbf{v}_k and $\mathbf{v}_{k'}$ are the operators of the velocities of the electrons in the molecule-fixed system, and \mathbf{s}_k is the spin momentum operator of the k th electron.

Introducing into (2) the momenta by $\mathbf{v}_k = \mathbf{p}_k/m$ we obtain

$$\mathbf{H}_a^{so} = \frac{he^2}{4\pi m^2 c^2} \sum_k \left\{ \left[\frac{Z_a}{r_{ka}^3} (\mathbf{r}_{ka} \times \mathbf{p}_k) + \frac{Z_b}{r_{kb}^3} (\mathbf{r}_{kb} \times \mathbf{p}_k) - \sum_{k'} \frac{1}{r_{kk'}^3} (\mathbf{r}_{kk'} \times (\mathbf{p}_k - 2\mathbf{p}_{k'})) \right] \mathbf{s}_k \right\} \quad (3)$$

Introducing the vectors \mathbf{r}_k (the radius vector of the k th electron as measured from the mass centre 0), and \mathbf{r} (the vector of the internuclear distance, pointing from nucleus a to nucleus b ; cf. Fig. 1.6) we may write

$$\mathbf{r}_{ka} = \mathbf{r}_k + \frac{\mu}{M_a} \mathbf{r}, \quad \mathbf{r}_{kb} = \mathbf{r}_k - \frac{\mu}{M_b} \mathbf{r} \quad (4)$$

where μ is the reduced mass of the molecule, and M_a (M_b) is the mass of nucleus a (b). Substitution of these into (3) yields the formula

$$\begin{aligned} \mathbf{H}_a^{so} = & \frac{he^2}{4\pi m^2 c^2} \sum_k \left(\left[\frac{Z_a}{\left| \mathbf{r}_k + \frac{\mu}{M_a} \mathbf{r} \right|^3} + \frac{Z_b}{\left| \mathbf{r}_k - \frac{\mu}{M_b} \mathbf{r} \right|^3} - \sum_{k'} \frac{1}{r_{kk'}^3} \right] (\mathbf{r}_k \times \mathbf{p}_k) + \right. \\ & + \left[\frac{\mu}{M_a} \frac{Z_a}{\left| \mathbf{r}_k + \frac{\mu}{M_a} \mathbf{r} \right|^3} - \frac{\mu}{M_b} \frac{Z_b}{\left| \mathbf{r}_k - \frac{\mu}{M_b} \mathbf{r} \right|^3} \right] (\mathbf{r} \times \mathbf{p}_k) + \\ & \left. + \sum_{k'} \frac{1}{r_{kk'}^3} [(\mathbf{r}_{k'} \times (\mathbf{p}_k - 2\mathbf{p}_{k'})) + 2(\mathbf{r}_k \times \mathbf{p}_{k'})] \mathbf{s}_k \right) \end{aligned} \quad (5)$$

Introducing the orbital angular momenta of the individual electrons by the relationship $\mathbf{l}_k = \mathbf{r}_k \times \mathbf{p}_k$, (5) becomes

$$\mathbf{H}_a^{so} = \sum_{kk'} a_{kk'} (\mathbf{l}_k \mathbf{s}_{k'}) = \sum_k a_k (\mathbf{l}_k \mathbf{s}_k) + \sum_{k' \neq k} a_{kk'} (\mathbf{l}_k \mathbf{s}_{k'}) \quad (6)$$

where by (5) $a_{kk'}$ is a function of the electron distances as measured from the origin of the coordinate system (r_k) of the inter-nuclear distance (r) and of the distances between the electrons ($r_{kk'}$). Fontana [51] has shown that, in the case of two outer valence electrons, if there is no change in the spin quantum number (i.e. if $\Delta S = 0$), then (6) becomes

$$\mathbf{H}_a^{so} = a'_1 (\mathbf{l}_1 \mathbf{S}) + a'_2 (\mathbf{l}_2 \mathbf{S}) \quad (7a)$$

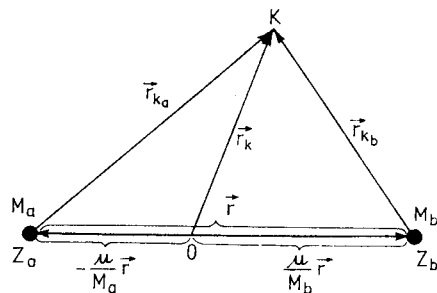


Fig. 1.6 Vector diagram of the k th electron orbiting around the nuclei.

and for $\Delta S = \pm 1$

$$\mathbf{H}_a^{so} = a_1''(\mathbf{l}_1 \mathbf{s}_1) + a_2''(\mathbf{l}_2 \mathbf{s}_2) \quad (7b)$$

where (in atomic units)

$$a_1' = \frac{\alpha^2}{4} \left[\frac{Z_a}{r_{1a}^3} + \frac{Z_b}{r_{1b}^3} - \frac{3}{r_{12}^3} \right] \quad (8a)$$

$$a_2' = \frac{\alpha^2}{4} \left[\frac{Z_a}{r_{2a}^3} + \frac{Z_b}{r_{2b}^3} - \frac{3}{r_{12}^3} \right]$$

$$a_1'' = \frac{\alpha^2}{2} \left[\frac{Z_a}{r_{1a}^3} + \frac{Z_b}{r_{1b}^3} + \frac{1}{r_{12}^3} \right] \quad (8b)$$

$$a_2'' = \frac{\alpha^2}{2} \left[\frac{Z_a}{r_{2a}^3} + \frac{Z_b}{r_{2b}^3} + \frac{1}{r_{12}^3} \right]$$

and α is the fine structure constant. Using the appropriate eigenfunctions, it can be shown that the matrix elements of (6) are different from zero only if, simultaneously, $\Delta S = 0, \pm 1$ and $\Delta \Omega = 0$, in such a way that either $\Delta A = \Delta \Sigma = 0$ or $\Delta A = -\Delta \Sigma = \pm 1$ (van Vleck [211]).

It is general practice to assume that (7a) holds for $\Delta S = 0$ and (7b) for $\Delta S = \pm 1$, also for more than two valence electrons, in the following form (van Vleck [212])

$$\mathbf{H}_a^{so} = \bar{A}(\mathbf{L}\mathbf{S}) \quad \Delta S = 0 \quad (9a)$$

$$\mathbf{H}_a^{so} = \sum_k \bar{a}_k(\mathbf{l}_k \mathbf{s}_k) \quad \Delta S = \pm 1 \quad (9b)$$

Writing (9a) in detail, we obtain

$$\mathbf{H}_a^{so} = \bar{A} \{ \mathbf{L}_\xi \mathbf{S}_\xi + \frac{1}{2} [(\mathbf{L}_\xi + i\mathbf{L}_\eta)(\mathbf{S}_\xi - i\mathbf{S}_\eta) + (\mathbf{L}_\xi - i\mathbf{L}_\eta)(\mathbf{S}_\xi + i\mathbf{S}_\eta)] \} \quad (10)$$

Since the eigenvalues of the operators \mathbf{L}_ξ and \mathbf{S}_ξ are A and Σ , respectively, and since $\mathbf{L}_\xi = \mp i\mathbf{L}_\eta$, we obtain by applying the relationship (1.2-17), to be proved below, to the matrix elements of (9a)

$$H_a^{so}(n, v, A, \Sigma; n, v, A, \Sigma) = \bar{A} \Delta \Sigma \quad (11a)$$

$$H_a^{so}(n, v, A, \Sigma; n', v', A \pm 1, \Sigma \mp 1) = (\bar{A} L_\xi)(n, v, A; n', v', A \pm 1) \times \\ \times \sqrt{S(S+1) - \Sigma(\Sigma \mp 1)} \quad (11b)$$

where

$$(\bar{A} L_\xi)(n, v, A; n', v', A \pm 1) = \sum_A \int \bar{\Phi}_{n,A}^* R_{n,v}^* \bar{A}(r) \mathbf{L}_\xi \bar{\Phi}_{n',A \pm 1} R_{n',v'} r^2 dr d\tau \quad (12)$$

In order to calculate the values of the matrix elements for the case $\Delta S = \pm 1$ one has to know the exact electron configuration and the forms of the corresponding eigenfunctions; these will be discussed in detail in Chapter 4.

(β) *Spin-Spin Interaction.* The second term of (1) can after Heisenberg [70] be written in the following form:

$$\mathbf{H}_a^{ss} = \frac{\hbar^2 e^2}{4\pi^2 m^2 c^2} \sum_{k' > k} \frac{-3(\mathbf{s}_k \mathbf{r}_{kk'}) (\mathbf{s}_{k'} \mathbf{r}_{kk'}) + (\mathbf{s}_k \mathbf{s}_{k'}) r_{kk'}^2}{r_{kk'}^5} \quad (13)$$

It was Kramers [132] and Hebb [68] who examined this expression in detail. Performing the operations indicated in (13) and forming the corresponding matrix elements from the electronic part of the eigenfunction (cf. (1.1-26)) we get

$$\begin{aligned} H_a^{ss}(n, A, \Sigma; n', A' \Sigma') = & \frac{\hbar^2 e^2}{4\pi^2 m^2 c^2} \sum_{k' > k} \{ (\bar{\zeta}_{kk'}^2 - \bar{\eta}_{kk'}^2) (s_{k\xi} s_{k'\xi} + s_{k\eta} s_{k'\eta} - 2s_{k\zeta} s_{k'\zeta}) \\ & - 3 \overline{\xi_{kk'} \eta_{kk'}} (s_{k\xi} s_{k'\eta} + s_{k\eta} s_{k'\xi}) - 3 \overline{\eta_{kk'} \zeta_{kk'}} (s_{k\eta} s_{k'\zeta} + s_{k\zeta} s_{k'\eta}) \\ & - 3 \overline{\zeta_{kk'} \xi_{kk'}} (s_{k\zeta} s_{k'\xi} + s_{k\xi} s_{k'\zeta}) \} \end{aligned} \quad (14)$$

where, for example,

$$\begin{aligned} \bar{\zeta}_{kk'}^2 &= \sum_A \sum_{A'} \int \bar{\Phi}_{n,A}^* R_{n,v}^* \frac{\xi_{kk'}^2}{r_{kk'}^5} \bar{\Phi}_{n',A'} R_{n',v'} r^2 dr d\tau \\ \overline{\xi_{kk'} \eta_{kk'}} &= \sum_A \sum_{A'} \int \bar{\Phi}_{n,A}^* R_{n,v}^* \frac{\xi_{kk'} \eta_{kk'}}{r_{kk'}^5} \bar{\Phi}_{n',A'} R_{n',v'} r^2 dr d\tau \end{aligned} \quad (15a)$$

and

$$(s_{k\xi} s_{k'\xi} + s_{k\eta} s_{k'\eta} - 2s_{k\zeta} s_{k'\zeta}) = \sum_{\Sigma} \sum_{\Sigma'} \chi_{\Sigma}^{A*} (s_{k\xi} s_{k'\xi} + s_{k\eta} s_{k'\eta} - 2s_{k\zeta} s_{k'\zeta}) \chi_{\Sigma'}^A \quad (15b)$$

and the other expressions have similar meanings.

Further analysis (Hebb [68]) has shown that the first term of (14) differs from zero only if $\Delta A = \Delta \Sigma = 0$, i.e. the diagonal elements of (14) are given. For the third and fourth terms, $\Delta A = -\Delta \Sigma = \pm 1$; this couples, e.g. the terms Π and Σ . Since, however, such terms, resulting from other interactions (e.g. spin-orbit interaction) are significantly greater, the terms resulting from spin-spin interaction are usually left out of consideration. For the second term, $\Delta A = -\Delta \Sigma = \pm 2$; this has no corresponding expression among other interaction terms, so that in certain cases, e.g. ${}^3\Pi_0$ ($A = +1$, $\Sigma = -1$) and ${}^3\Pi_0$ ($A = -1$, $\Sigma = +1$), the interaction takes place via the second term, as revealed among others by the fact that the A -type doubling is in general stronger in the ${}^3\Pi_0$ state than in the others (cf. (2.1.4-31) and (2.1.4-33)).

Kramers [132] has shown that the behaviour of (14) is in every respect identical to that of the expressions formed using the resultant spin momentum \mathbf{S} of the electrons so that, apart from a constant factor, (14) can be replaced by the latter. Accordingly, the following can be written instead of (14):

$$H_a^{ss}(n, v, A, \Sigma; n, v, A, \Sigma) = \bar{\varepsilon}(n, v, A; n, v, A) (2S_{\xi}^2 - S_{\xi}^2 - S_{\eta}^2)_{\Sigma, \Sigma} \quad (16a)$$

$$H_a^{ss}(n, v, A, \Sigma; n', v', A \pm 1, \Sigma \mp 1) = \bar{\beta}(n, v, 1; n', v', A \pm 1) \times \\ \times (S_\eta S_\zeta + S_\zeta S_\eta)_{\Sigma, \Sigma \mp 1} \quad (16b)$$

$$H_a^{ss}(n, v, A, \Sigma; n', v', A \pm 2, \Sigma \mp 2) = \bar{\alpha}(n, v, A; n', v', A \pm 2) \times \\ \times (S_\xi S_\eta + S_\eta S_\xi)_{\Sigma, \Sigma \mp 2} \quad (16c)$$

By the well-known relationships

$$(S^2)_{\Sigma, \Sigma} = S(S+1); \quad (S_\zeta)_{\Sigma, \Sigma} = \Sigma \\ (S_\xi)_{\Sigma, \Sigma \pm 1} = \frac{1}{2} \sqrt{(S \pm \Sigma + 1)(S \mp \Sigma)} \\ (S_\eta)_{\Sigma, \Sigma \pm 1} = \pm \frac{i}{2} \sqrt{(S \pm \Sigma + 1)(S \mp \Sigma)} \quad (17)$$

(see e.g. Heisenberg and Jordan [71]), we obtain for (16a), (16b) and (16c)

$$H_a^{ss}(n, v, A, \Sigma; n, v, A, \Sigma) = \bar{\varepsilon}(n, v, A; n, v, A) [3\Sigma^2 - S(S+1)] \quad (18a)$$

$$H_a^{ss}(n, v, A, \Sigma; n', v', A \pm 1, \Sigma \mp 1) = \bar{\beta}(n, v, A; n', v', A \pm 1) (2\Sigma \mp 1) \times \\ \times \sqrt{(S \mp \Sigma + 1)(S \pm \Sigma)} \quad (18b)$$

$$H_a^{ss}(n, v, A, \Sigma; n', v', A \pm 2, \Sigma \mp 2) = \frac{1}{2} |\bar{\alpha}(n, v, A; n', v', A \pm 2)| \times \\ \times \sqrt{(S \mp \Sigma + 1)(S \pm \Sigma)(S \mp \Sigma + 2)(S \pm \Sigma - 1)} \quad (18c)$$

(γ) *Spin-Rotation Interaction.* The third term of (1) has no counterpart in the expression for atoms. It was Kramers [132] who first pointed out that since (2) contains the velocities of the electrons as well, the magnetic field set up by the rotation of the nuclei affects the electron spins also in another way, not dealt with so far, which gives rise to a new term in the perturbation potential (1). For the coordinate system fixed to the nuclei, i.e. for case *a*, this term was derived by Kovács [108].

The connexion between space-fixed and molecule-fixed systems is described by (1.1-2) and (1.1-3). Because of the rotation of the molecule, not only the x, y, z -components in (1.1-3) but also the angles θ and ω are time-dependent in the expressions of the electron velocities. If the components thus calculated of the velocity of the k th electron are denoted $\dot{\xi}_{sk}, \dot{\eta}_{sk}, \dot{\zeta}_{sk}$, whereas $\dot{\xi}_{mk}, \dot{\eta}_{mk}, \dot{\zeta}_{mk}$ denote the components in a non-rotating molecule-fixed system (or, in other words, they denote the molecule-fixed components of the real velocities measured in a system, at rest in space), then the change in the velocity components introduced by the rotation of the molecule will by (1.1-2) and (1.1-3) assume the form

$$\Delta \dot{\xi}_k = \dot{\xi}_{mk} - \dot{\xi}_{sk} = \zeta_k \sin \theta \dot{\omega} \\ \Delta \dot{\eta}_k = \dot{\eta}_{mk} - \dot{\eta}_{sk} = -\zeta_k \dot{\theta} \\ \Delta \dot{\zeta}_k = \dot{\zeta}_{mk} - \dot{\zeta}_{sk} = -\xi_k \sin \theta \dot{\omega} + \eta_k \dot{\theta} \quad (19)$$

This follows from the fact that, owing to the possible rotation in the $\xi\eta$ plane, $-\eta_k \cos \theta \dot{\omega}$ and $\xi_k \cos \theta \dot{\omega}$ also contribute to $\dot{\xi}_{sk}$ and $\dot{\eta}_{sk}$, respectively. Consequently, by (19) we now write in formula (5) $\mathbf{v}_{mk} = \mathbf{v}_{sk} + \Delta \mathbf{v}_k$ instead of $\mathbf{p}_k/m = \mathbf{v}_k$. Additional terms appearing in the first part of (5) are

$$[-\eta_k \xi_k \sin \theta \dot{\omega} + (\eta_k^2 + \xi_k^2) \dot{\theta}] \mathbf{s}_{k\xi} + [(\xi_k^2 + \eta_k^2) \sin \theta \dot{\omega} - \xi_k \eta_k \dot{\theta}] \mathbf{s}_{k\eta} - [\xi_k \zeta_k \dot{\theta} + \eta_k \zeta_k \sin \theta \dot{\omega}] \mathbf{s}_{k\zeta} \quad (20)$$

Similar expressions are obtained also from the other terms.

In the calculation of the matrix elements of (20), a term diagonal in n, v, A, S is obtained only from the second and third terms. It is

$$H_a^{sr} = \sum_k m a_k \frac{\xi_k^2 + \eta_k^2}{I} (R_\xi s_{k\xi} + R_\eta s_{k\eta}) \quad (21)$$

where

$$\begin{aligned} R_\xi &= I\theta \\ R_\eta &= I \sin \theta \dot{\omega} \end{aligned} \quad (22)$$

are the ξ and η components, respectively, of the rotational angular momentum of the molecule; I is its moment of inertia, and

$$\begin{aligned} a_k \frac{\xi_k^2 + \eta_k^2}{I} &= \sum_A \int \bar{\Phi}_{n,A}^* R_{n,v}^* a_k(r_k, r) \frac{\xi_k^2 + \eta_k^2}{I} \bar{\Phi}_{n,A} R_{n,v} r^2 dr d\tau \\ (R_\xi s_{k\xi} + R_\eta s_{k\eta}) &= \sum_\Sigma \sum_{\Sigma'} \chi_\Sigma^{A*} (\mathbf{R}_\xi \mathbf{s}_{k\xi} + \mathbf{R}_\eta \mathbf{s}_{k\eta}) \chi_{\Sigma'}^A \end{aligned} \quad (23)$$

Kramers [132] has shown that, apart from a constant factor, an expression of the form (21) behaves identically to a similar expression formed from the components of the resultant spin momentum of the electrons; (21) can therefore be replaced by

$$H_a^{sr}(n, v, A, \Sigma; n, v, A, \Sigma') = \bar{\gamma}(n, v, A; n, v, A) (R_\xi S_\xi + R_\eta S_\eta)_{\Sigma\Sigma'} \quad (24)$$

Since, however, the rotational angular momentum of the molecule is not quantized in case a , we can rewrite Formula (24) to read

$$\{H_a^{sr} = \bar{\gamma}[(R_\xi + S_\xi) S_\xi + (R_\eta + S_\eta) S_\eta + S_\xi^2 - S_\eta^2]_{\Sigma\Sigma'} \quad (25)$$

Since L_ξ and L_η have no diagonal elements in A , one can simply add L_ξ and L_η to $R_\xi + S_\xi$ and $R_\eta + S_\eta$, respectively, in which case the two sums will be identical with the ξ and η component, respectively, of the quantized total angular momentum of the molecule; hence,

$$\begin{aligned} H_a^{sr} &= \bar{\gamma}(S_\xi^2 - S_\eta^2 + J_\xi S_\xi + J_\eta S_\eta)_{\Sigma\Sigma'} = \bar{\gamma} \{ S_\xi^2 - S_\eta^2 + \frac{1}{2} [(J_\xi + iJ_\eta)(S_\xi - iS_\eta) \\ &\quad + (J_\xi - iJ_\eta)(S_\xi + iS_\eta)] \}_{\Sigma\Sigma'} \end{aligned} \quad (26)$$

For the first two terms in (26) $\Delta\Sigma = 0$; for the other two terms, $\Delta\Sigma = \pm 1$. By (17) and by (1.3-6) below, the explicit forms of the matrix elements are

$$H_a^{sr}(n, v, A, \Sigma; n, v, A, \Sigma) = \bar{\gamma}(n, v, A; n, v, A) [\Sigma^2 - S(S+1)] \quad (27a)$$

$$H_a^{sr}(n, v, A, \Sigma; n, v, A, \Sigma \pm 1) = -1/2 \bar{\gamma}(n, v, A; n, v, A) \times [J(J+1) - \Omega(\Omega \pm 1)]^{1/2} [S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2} \quad (27b)$$

The energy terms and perturbation-matrix elements considered thus far in the electron spin interactions in *Hund's case a*, are provided by the *Hamilton operator* of the electronic part of the wave equation.

Case b. In Equation (1.1-22), the operator \mathbf{H}_b' of the electronic part also contains the interaction operators for the spin, but since in this case the interaction between the rotation of the molecule and the electron spin is weak (unable to follow the fast rotation, the spin vectors are lagging behind), it is appropriate to express these operators in the space-fixed coordinate system:

$$\mathbf{H}_b^s(s_i) = \mathbf{H}_b^{so} + \mathbf{H}_b^{ss} + \mathbf{H}_b^{sr} \quad (28)$$

Let us now examine these separately.

(α) *Spin-Orbit Interaction.* According to van Vleck [215], the form of the spin-orbit interaction in the space-fixed coordinate system differs from (2) in that, apart from the velocities of the electrons, referred to the space-fixed system, the velocities of the nuclei are also to be taken into account. Then,

$$\mathbf{H}_b^{so} = \frac{\hbar e^2}{4\pi m c^2} \sum_k \left\{ \sum_i \frac{Z_i}{r_{ki}^3} [\mathbf{r}_{ki} \times (\mathbf{v}_k - 2\mathbf{v}_i)] - \sum_{k' > k} \frac{1}{r_{kk'}^3} [\mathbf{v}_{kk'} \times (\mathbf{v}_k - 2\mathbf{v}_{k'})] \right\} \mathbf{s}_k \quad (29)$$

where the possible values of i are 1, 2; \mathbf{v}_i is the velocity of the nuclei in the space-fixed system. The remainder of the notation is as that in (2), with the difference that the velocities of the electrons are also taken in the space-fixed system.

If, for the time being, the terms containing the velocities of the nuclei are disregarded, Formula (29) can be treated in much the same way as (2); the matrix elements of the relationships

$$\mathbf{H}_b^{so} = \sum_{k'} a_{kk'}(\mathbf{l}_k \mathbf{s}_{k'}) = \sum_k a_k(\mathbf{l}_k \mathbf{s}_k) + \sum_{k' \neq k} a_{kk'}(\mathbf{l}_k \mathbf{s}_{k'}) \quad (30)$$

can be calculated according as there are one, two or three valence electrons outside the closed shell. In order to obtain general expressions for $\Delta S = 0$ and $\Delta A = 0$, it is usual to replace (30) by an interaction of the following form:

$$\mathbf{H}_b^{so} = \bar{A} \{ \mathbf{L}_\zeta \mathbf{S}_\zeta + 1/2 [(\mathbf{L}_\xi + i\mathbf{L}_\eta)(\mathbf{S}_\xi - i\mathbf{S}_\eta) + (\mathbf{L}_\xi - i\mathbf{L}_\eta)(\mathbf{S}_\xi + i\mathbf{S}_\eta)] \} \quad (31)$$

The first term of (31) can be written according to Hill and van Vleck [77] as

$$\bar{A} \mathbf{L}_\zeta \mathbf{S}_\zeta = \bar{A}(\Delta \mathbf{S}) = \bar{A}[(\Delta_\parallel \mathbf{S}) + (\Delta_\perp \mathbf{S})] \quad (32)$$

where \mathbf{A} , the component in the direction of the inter-nuclear axis of the resultant orbital angular momentum of the electrons, is split into two components; one is parallel, the other is perpendicular to the vector \mathbf{N} . Of these two terms, it is the former that provides those elements for which, in addition to $\Delta S = 0$ and $\Delta A = 0$, also $\Delta N = 0$; for the second term $\Delta N = \pm 1$. For these, Hill and van Vleck [77] have found

$$H_b^{so}(n, J, S, A, N; n, J, S, A, N) = \bar{A} A^2 \frac{[J(J+1) - N(N+1) - S(S+1)]}{2N(N+1)} \quad (33a)$$

$$\begin{aligned} H_b^{so}(n, J, S, A, N; n, J, S, A, N+1) \\ = \bar{A} A \{[(N+1)^2 - A^2][J+N+1)(J+N+2) - S(S+1)]\}^{1/2} \times \\ \times \frac{[S(S+1) - (J-N)(J-N-1)]^{1/2}}{2(N+1)[(2N+1)(2N+3)]^{1/2}} \end{aligned} \quad (33b)$$

Suitable substitutions of A and S in the formulas (33a) and (33b) give the case b interaction energy and its perturbation-matrix elements for terms of any type and multiplicity.

Fontana [51] has found that for the case of two outer (valence) electrons the rigorous form of (30) for $\Delta N = 0$ yields an expression similar to (33a):

$$\begin{aligned} H_b^{so}(n, J, 1, A, N; n, J, 1, A, N) \\ = \sum_{k=1}^2 (a'_k l_{k\zeta})(n, A; n, A) \frac{A[J(J+1) - N(N+1) - 2]}{2N(N+1)} \end{aligned} \quad (34a)$$

According to Lue-Yung Chow Chiu [37] the result is similar to that for $\Delta N = \pm 1$:

$$\begin{aligned} H_b^{so}(n, J, 1, A, N; n, J, 1, A, N+1) = \sum_{k=1}^2 (a'_k l_{k\zeta})(n, A; n, A) \times \\ \times \frac{\{[(N+1)^2 - A^2][J+N+1)(J+N+2) - 2][2 - (J-N)(J-N-1)]\}^{1/2}}{2(N+1)[(2N+1)(2N+3)]^{1/2}} \end{aligned} \quad (34b)$$

In both cases the $\Sigma(a'_k l_{k\zeta})$ replacing $\bar{A} A$ can be determined from the appropriate eigenfunctions by

$$\Sigma(a'_k l_{k\zeta})(n, A; n, A) = \sum_A \int \bar{\Phi}_{n,A}^* (a'_1 \mathbf{l}_{1\zeta} + a'_2 \mathbf{l}_{2\zeta}) \bar{\Phi}_{n,A} d\tau \quad (35)$$

Likewise, according to Lue-Yung Chow Chiu [37], the second term of (31) yields for $S = 1$, $\Delta A = \pm 1$ and $\Delta N = 0, \pm 1$

$$\begin{aligned} H_b^{so}(n, J, 1, A, N; n', J, 1, A+1, N) = \sum_{k=1}^2 (a'_k l_{k\zeta})(n, A; n', A+1) \times \\ \times \frac{N(N+1) - J(J+1) + 2}{4N(N+1)} [(N-A)(N+A+1)]^{1/2} \end{aligned} \quad (36a)$$

$$H_b^{so}(n, J, 1, A, N; n', J, 1, A+1, N+1) = \sum_{k=1}^2 (a'_k l_k^-)(n, A; n', A+1) \times \\ \times \left[\frac{(J+N+3)(J+N)(N-J+2)(J-N+1)(N+A+1)(N+A+2)}{16(N+1)^2(2N+1)(2N+3)} \right]^{1/2} \quad (36b)$$

$$H_b^{so}(n, J, 1, A, N; n', J, 1, A+1, N-1) = \sum_{k=1}^2 (a'_k l_k^-)(n, A; n', A+1) \times \\ \times \left[\frac{(J+N+2)(N-J+1)(J+N-1)(J-N+2)(N-A-1)(N-A)}{16N^2(2N-1)(2N+1)} \right]^{1/2} \quad (36c)$$

Using

$$l_k^- = l_{k\xi} - i l_{k\eta} \quad (37)$$

and applying appropriate eigenfunctions, one finds that

$$\sum_{k=1}^2 (a'_k l_k^-)(n, A; n', A+1) = \sum_A \bar{\Phi}_{n,A}^* (a'_1 l_1^- + a'_2 l_2^-) \bar{\Phi}_{n',A+1} d\tau \quad (38)$$

The matrix elements (36) were first given for actual cases by Kovács [101] who derived them from case *a*.

In addition to the foregoing interactions between terms of the same multiplicity (i.e. for $\Delta S = 0$), Lue-Yung Chow Chiu [37] gave for two outer electrons also the matrix elements for interactions between terms of different multiplicity (i.e. for $\Delta S = \pm 1$). In this case (30) assumes the form (9b) with coefficients given by (8b). The appropriate matrix elements are

$$H_b^{so}(n, J, 0, A, N; n', J, 1, A, N) = \sum_{k=1}^{2'} (a''_k l_{k\xi})(n, A; n', A) \times \\ \times [(J+N+2)(N-J+1)(J-N+1)(J+N)]^{1/2} \frac{A}{4N(N+1)} \quad (39a)$$

$$H_b^{so}(n, J, 0, A, N; n', J, 1, A, N+1) = \sum_{k=1}^2 (a''_k l_{k\xi})(n, A; n', A) \times \\ \times \left[\frac{(J+N+3)(J+N+2)(N-J+2)(N-J+1)[(N+1)^2 - A^2]}{16(N+1)^2(2N+1)(2N+3)} \right]^{1/2} \quad (39b)$$

$$H_b^{so}(n, J, 0, A, N; n', J, 1, A+1, N) = \sum_{k=1}^2 (a''_k l_k^-)(n, A; n', A+1) \times \\ \times \frac{[(J+N+2)(N-J+1)(J-N+1)(J+N)(N+A+1)(N-A)]^{1/2}}{8N(N+1)} \quad (39c)$$

$$H_b^{so} (n, J, 0, A, N; n', J, 1, A + 1, N + 1) = \sum_{k=1}^2 (a_k'' l_k^-) (n, A; n', A + 1) \times \\ \times \left[\frac{(J + N + 3)(J + N + 2)(N - J + 2)(N - J + 1)(N + A + 1)(N + A + 2)}{64(N + 1)^2(2N + 1)(2N + 3)} \right]^{1/2} \quad (39d)$$

$$H_b^{so} (n, J, 0, A, N; n', J, 1, A + 1, N - 1) = \sum_{k=1}^2 (a_k'' l_k^-) (n, A; n', A + 1) \times \\ \times \left[\frac{(J + N)(J + N - 1)(J - N + 2)(J - N + 1)(N - A - 1)(N - A)}{64N^2(2N - 1)(2N + 1)} \right]^{1/2} \quad (39e)$$

where the coefficients can be obtained from

$$\sum_{k=1}^2 (a_k'' l_{k\zeta}) (n, A; n', A) = \sum_A \int \bar{\Phi}_{n,A}^* (a_1'' \mathbf{l}_{1\zeta} - a_2'' \mathbf{l}_{2\zeta}) \bar{\Phi}_{n',A} d\tau \quad (40)$$

$$\sum_{k=1}^2 (a_k'' l_k^-) (n, A; n', A + 1) = \sum_A \int \bar{\Phi}_{n,A}^* (a_1'' \mathbf{l}_1^- - a_2'' \mathbf{l}_2^-) \bar{\Phi}_{n',A+1} d\tau$$

As is apparent in (40), the bar over the summation symbol means that the two terms should be subtracted from each other instead of being added. Formulas (39) were also derived by Kovács [101] and likewise from case *a*.

In considering the motions of the nuclei we can average the motions of the electrons since the latter move much quicker than the former. The terms obtained in this way are the same as those determined later in section (γ) [211, 205].

(β) *Spin-Spin Interaction.* The operator of the spin-spin interaction is of the same form as that in case *a*, i.e. as (13), although in the present case the electron-spin operators and the coordinates are expressed in the space-fixed system. The matrix elements are given for case *b* by Fontana [51] and Lue-Yung Chow Chiu [37]. The elements with $\Delta N = 0$ and $\Delta A = 0, \pm 1, \pm 2$ are the following:

$$H_b^{ss} (n, J, S, A, N; n, J, S, A', N) = \frac{3/4 C(C + 1) - N(N + 1)S(S + 1)}{(2N - 1)N(N + 1)(2N + 3)} F \quad (41)$$

where

$$C = J(J + 1) - N(N + 1) - S(S + 1) \quad (42)$$

and

$$F = 2\bar{\epsilon}[3A^2 - N(N + 1)] \quad \text{for } A' = A \quad (43a)$$

$$F = \bar{\beta}(2A - 1)[(N - A + 1)(N + A)]^{1/2} \quad \text{for } A' = A - 1 \quad (43b)$$

$$F = \bar{\alpha}[(N + A - 1)(N + A)(N - A + 1)(N - A + 2)]^{1/2} \\ \text{for } A' = A - 2 \quad (43c)$$

There are, in addition, matrix elements for the case $\Delta N = \pm 1$, and, in the case $J = N + 1$, also for $\Delta N = \pm 2$. (See Lue-Yung Chow Chiu [37].)

(γ) *Spin-Rotation Interaction.* The magnetic field caused by the rotation of the molecule interacts with the electron spins. This interaction can be determined if one takes into account, when calculating the velocities of the electrons by (1.1-2), the fact that besides ξ , η , ζ , the quantities θ and ω are also time-dependent. Then, according to Kramers [132], the change in the velocity of the electron arising from the rotation of the nuclei will be given by

$$\begin{aligned}\Delta\dot{x} &= (\zeta \cos \theta + \eta \sin \theta) \cos \omega \dot{\theta} - (\zeta \sin \omega + \xi \sin \theta \cos \omega) \sin \theta \dot{\omega} \\ \Delta\dot{y} &= (\zeta \cos \theta + \eta \sin \theta) \sin \omega \dot{\theta} + (\zeta \cos \omega - \xi \sin \theta \sin \omega) \sin \theta \dot{\omega} \\ \Delta\dot{z} &= (-\zeta \sin \theta + \eta \cos \theta) \dot{\theta} - \xi \sin \theta \cos \omega \dot{\omega}\end{aligned}\quad (44)$$

Then, as it can be shown by writing out in detail, $\dot{\xi}$ and $\dot{\eta}$ are complemented by the terms $-\eta \cos \theta \dot{\omega}$ and $\xi \cos \theta \dot{\omega}$, respectively, to account for the possibility of rotation in the $\xi\eta$ plane.

In Formula (2) the velocities \mathbf{v}_k of the electrons as expressed in the space-fixed system will be composed of the velocities in the molecule-fixed system, on the one hand (when ξ , η , ζ are the only time-dependent quantities) and, on the other, of terms arising from the rotation of the molecule, as calculated from (44): $\mathbf{v}_k = \mathbf{v}_{km} + \Delta\mathbf{v}_k$. Consequently, a correction term is to be added to (30): it can be written according to Kramers [132] as

$$\mathbf{H}_b^{sr} = \gamma(\mathbf{R}_x \mathbf{S}_x + \mathbf{R}_y \mathbf{S}_y + \mathbf{R}_z \mathbf{S}_z) = \gamma(\mathbf{R}\mathbf{S}) \quad (45)$$

where \mathbf{R} is the rotational angular momentum of the molecule. If $A = 0$, this momentum is quantized and identical to \mathbf{N} . This form (given by Kramers) is generally used also when $A \neq 0$. Rigorous calculation yields that if $A \neq 0$ then $\mathbf{R} \neq \mathbf{N}$ ($\mathbf{R} = \mathbf{N} - \mathbf{L}$), or (neglecting the components \mathbf{L}_ξ and \mathbf{L}_η , which do not give diagonal terms in A , and putting $\mathbf{L}_\zeta = \mathbf{N}_\zeta$) $\mathbf{R} = \mathbf{N} - \mathbf{N}_\zeta$. Substituting this into (45) yields

$$\mathbf{H}_b^{sr} = \bar{\gamma}[(\mathbf{N} - \mathbf{N}_\zeta)\mathbf{S}] = \bar{\gamma}[(\mathbf{N}\mathbf{S}) - (\mathbf{N}_\zeta\mathbf{S})] = \bar{\gamma}[(\mathbf{N}\mathbf{S}) - (A\mathbf{S})] \quad (46)$$

which by (32) and (33) can be written as

$$\begin{aligned}H_b^{sr}(n, A, J, N; n, A, J, N) \\ = \frac{1}{2}\bar{\gamma}[J(J+1) - N(N+1) - S(S+1)] \left[1 - \frac{A^2}{N(N+1)} \right]\end{aligned}\quad (47)$$

It is to be noted that, with increasing N , the last term converges to zero very fast, so that no great error is committed if one takes instead of (47) the simpler form given by Kramers [132] for $A = 0$, i.e. for the Σ terms.

In the above discussion, we have derived those energy terms and perturbation-matrix elements which are provided by the *Hamilton* operator of the electronic part of the wave equation, if the electron spin interactions are taken into account according to *Hund's case b*.

In Formulas (1.1-24a) and (1.1-24b) and in the similar wave equations for *Hund's case b* the terms arising from $\mathbf{H}_a^s(\sigma_i)$ and $\mathbf{H}_b^s(s_i)$, respectively, should be separately recorded, together with the electron energies (1.1-32). This is largely due to the fact that (1.1-32) refers only to that part of (1.1-14) which does not contain the spin, as well as the fact that the terms mentioned above and the diagonal matrix elements connected with them play an important role in forming the multiplet structure of the terms in *Hund's* limiting cases *a* and *b* and in the intermediate case between them.

1.3. MATRIX ELEMENTS ARISING FROM THE TERMS NEGLECTED ON THE SEPARATION OF THE WAVE EQUATION

As can be seen in the previous section, in *Hund's case a*, the resultant spin momentum \vec{S} of the electrons is coupled to the inter-nuclear axis, whereas in case *b* it is coupled to the vector \vec{N} . A molecule in slow rotation generally approximates the first case, whereas for increased rotation the second case provides a better approximation. It is also evident that as the molecule gradually passes from a state of slow rotation (with low values of the rotational quantum number J) to one of increased rotation (with higher values of J), the decoupling of the spin momentum from the molecular axis and its coupling to the vector \vec{N} also takes place gradually. In a quantum-mechanical treatment of this gradual change the spin-dependent parts of (1.1-27a) and (1.1-27b) that are neglected on separation should also be taken into account.

It follows from the above discussion that, although the resultant orbital angular momentum \vec{L} is far more strongly coupled to the inter-nuclear axis than the spin momentum \vec{S} (i.e. it has a higher bond energy), the increasing rotation must have some effect upon \vec{L} , too. It happens indeed, particularly in light molecules, that if the axial field along the inter-nuclear axis is not very strong, strong rotation results in the de-coupling of the vector \vec{L} from the inter-nuclear axis; \vec{L} is then coupled to the axis of rotation. This is *Hund's case d* (Fig. 1.7). This incipient de-coupling of the vector \vec{L} is not, however, restricted to light molecules, indeed it is quite a frequent phenomenon. It results in the splitting of the two de-generate states of different symmetry arising from the orientations $+A$ and $-A$; this is the previously mentioned *A-type splitting* or *A-type doubling*. It can therefore be stated that *A-type doubling* reflects an early stage of the gradual transition from case *a* or case *b* to case *d*. For the quantum-mechanical treatment of this

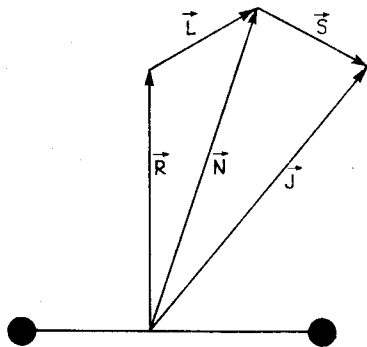


Fig. 1.7 Vector model of *Hund's case d*.

gradual transition, on the basis of perturbation theory, the parts depending on the orbital angular momentum \vec{L} of the terms neglected on the separation of (1.1-21) and (1.1-22) are also used.

Case a. Let us study these terms first in connexion with case *a* (Formula (1.1-27a)). Let us put

$$H_{1a}^p(n, v, \Omega, J; n', v', \Omega', J') = \int \psi_{n,v,\Omega,J}^* \mathbf{H}_{1a}^p \psi_{n',v',\Omega',J'} d\tau = H_{1a}^p \quad (1)$$

where \mathbf{H}_{1a}^p is to be taken from (1.1-27a) and the eigenfunctions are to be taken from (1.1-23). It can be shown that (1) is different from zero only if $\Omega' = \Omega \pm 1$ and $J' = J$. Then, since

$$P_\xi = \mp i P_\eta \quad (2)$$

we have

$$H_{1a}^p = \pm i \left\{ \pm \frac{\partial}{\partial \theta} + \frac{i}{\sin \theta} \frac{\partial}{\partial \omega} + (\Omega \pm 1) \cot \theta \right\} 2(\bar{B}P_\xi)_{\Omega, \Omega \pm 1} \quad (3)$$

where we have made use of

$$P_\eta P_\zeta + P_\zeta P_\eta = \pm i(2\Omega \pm 1) P_\xi \quad (4)$$

since $P_\zeta = \Omega$. In (3), $\bar{B} = \hbar^2/8\pi^2\mu r^2$. The first part of (3) contains only the rotational part $u_{J,\Omega,M}(\theta, \omega)$ of the eigenfunction (1.1-23); it is the second part that contains the electronic and vibrational parts, i.e. $\Phi_{n,\Omega} R_{n,v}$. The first part of (3) can easily be expressed in terms of the total angular momentum operator of the molecule (Gol'dman and Krivchenkov [3], pp 218-24) as

$$\left\{ \pm \frac{\partial}{\partial \theta} + \frac{i}{\sin \theta} \frac{\partial}{\partial \omega} + (\Omega \pm 1) \cot \theta \right\}_{\Omega, \Omega \pm 1} = \pm i(J_\xi \pm iJ_\eta)_{\Omega, \Omega \pm 1} \quad (5)$$

For these, the following relations hold:

$$(J^2)_{\Omega, \Omega} = J(J+1); (J_\zeta)_{\Omega, \Omega} = \Omega \quad (6)$$

$$(J_\xi \pm iJ_\eta)_{\Omega, \Omega \pm 1} = -\sqrt{J(J+1) - \Omega(\Omega \pm 1)}$$

The line of thought leading up to (5) is as follows. The angular momentum operator \mathbf{J}_ξ of rotation in the plane perpendicular to the ξ axis can be written as

$$\mathbf{J}_\xi = -i \frac{\partial}{\partial \alpha} \quad (7)$$

where α is the angle of rotation in the plane perpendicular to the ξ axis. Since a rotation by $d\alpha$ of the coordinate system ξ, η, ζ around the axis ξ changes the angles describing the position of the system ξ, η, ζ with respect to the system x, y, z (cf. (1.1-1)),

$$\mathbf{J}_\xi = -i \left(\frac{\partial}{\partial \theta} \frac{\partial \theta}{\partial \alpha} + \frac{\partial}{\partial \varphi} \frac{\partial \varphi}{\partial \alpha} + \frac{\partial}{\partial \psi} \frac{\partial \psi}{\partial \alpha} \right) \quad (8)$$

For an infinitesimal rotation $d\alpha$ around the axis ξ

$$\begin{aligned} \xi &= \xi' \\ \eta &= \eta' - \zeta' d\alpha \\ \zeta &= \zeta' + \eta' d\alpha \end{aligned} \quad (9)$$

and by (1.1-1)

$$z = \xi' \sin(\varphi + d\varphi) \sin(\theta + d\theta) + \eta' \cos(\varphi + d\varphi) \sin(\theta + d\theta) + \zeta' \cos(\theta + d\theta) \quad (10)$$

On the other hand, substituting (9) into (1.1-1) we obtain

$$z = \xi' \sin \varphi \sin \theta + \eta' (\cos \varphi \sin \theta + \cos \theta d\alpha) + \zeta' (\cos \theta - \cos \varphi \sin \theta d\alpha) \quad (11)$$

The comparison of the above two equations yields

$$\frac{d\theta}{d\alpha} = \cos \varphi; \quad \frac{d\varphi}{d\alpha} = -\sin \varphi \cot \theta \quad (12)$$

and similarly,

$$\frac{d\psi}{d\alpha} = \frac{\sin \varphi}{\sin \theta}$$

By these relations, the corresponding expressions for (8) and for the other two operators turn out to be

$$\begin{aligned} \mathbf{J}_\xi &= -i \left(\cos \varphi \frac{\partial}{\partial \theta} - \sin \varphi \cot \theta \frac{\partial}{\partial \varphi} + \frac{\sin \varphi}{\sin \theta} \frac{\partial}{\partial \psi} \right) \\ \mathbf{J}_\eta &= -i \left(-\sin \varphi \frac{\partial}{\partial \theta} - \cos \varphi \cot \theta \frac{\partial}{\partial \varphi} + \frac{\cos \varphi}{\sin \theta} \frac{\partial}{\partial \psi} \right) \\ \mathbf{J}_\zeta &= -i \frac{\partial}{\partial \varphi} \end{aligned} \quad (13)$$

Substituting $\varphi = 0$, $\theta = \theta$ and $\psi = \omega + \frac{\pi}{2}$ according to (1.1-2), and considering that

$\mathbf{J}_\zeta = \mathbf{P}_\zeta$, we have

$$\mathbf{J}_\xi \pm i \mathbf{J}_\eta = \mp i \left[\pm \frac{\partial}{\partial \theta} + \frac{i}{\sin \theta} \frac{\partial}{\partial \omega} + \cot \theta \mathbf{P}_\zeta \right] \quad (14)$$

whence (5) is directly obtained by taking into account that $\mathbf{P}_\zeta \Phi_{\Omega \pm 1} = (\Omega \pm 1) \Phi_{\Omega \pm 1}$

By (13), clearly,

$$\begin{aligned} \mathbf{J}_\xi \mathbf{J}_\eta - \mathbf{J}_\eta \mathbf{J}_\xi &= -i \mathbf{J}_\zeta \\ \mathbf{J}_\eta \mathbf{J}_\zeta - \mathbf{J}_\zeta \mathbf{J}_\eta &= -i \mathbf{J}_\xi \\ \mathbf{J}_\zeta \mathbf{J}_\xi - \mathbf{J}_\xi \mathbf{J}_\zeta &= -i \mathbf{J}_\eta \end{aligned} \quad (15)$$

which shows that, for the operators of the components of the angular momentum as expressed in the coordinates of the rotating system, commutation relations having signs opposite to those in the fixed system are valid. Hence, the behaviour of (6) is the converse of those of the operators of the orbital angular momentum and of the electron spin, the latter being functions only of the internal coordinates (i.e. of the system fixed to the molecule). In the fixed system, Equations (15) are valid, of course, with the usual (positive) sign.

Using (5) and (6), expression (3) can be rewritten in the form

$$\begin{aligned} &H_{1a}^p(n, v, \Omega, J; n', v', \Omega \pm 1, J) \\ &= 2(\bar{B}P_\xi)(n, v, \Omega; n', v', \Omega \pm 1) \sqrt{J(J+1) - \Omega(\Omega \pm 1)} \end{aligned} \quad (16)$$

where

$$(\bar{B}P_\xi)(n, v, \Omega; n', v', \Omega \pm 1) = \int \Phi_{n,\Omega}^* R_{n,v}^* \bar{B}P_\xi \Phi_{n',\Omega \pm 1} R_{n',v'} d\tau \quad (17)$$

Incidentally, Formulas (16) and (27) below can, according to Ying-Nan Chiu [35], be simply obtained by vector algebra from the wave equation of the molecule. Let

$$\bar{B}(r)\mathbf{R}^2 = -\frac{\hbar^2}{8\pi^2\mu r^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\omega^2} \right] \quad (18)$$

which, the part of the wave equation (1.1-7) of the molecule that depends on the angles describing the relative positions of the two coordinate systems, is nothing else, apart from the factor outside the bracket, than the square of the total angular momentum operator referring to the rigid rotation of the nuclei (\mathbf{R}^2). Taking into account the electron spin, we may write

$$\begin{aligned} \bar{B}(r)\mathbf{R}^2 &= \bar{B}(\mathbf{J} - \mathbf{P})^2 = \bar{B}[\mathbf{J}^2 + \mathbf{P}^2 - 2(\mathbf{JP})] = \bar{B}[(\mathbf{J}^2 - 2\mathbf{J}_\zeta\mathbf{P}_\zeta + \mathbf{P}_\zeta^2) - \\ &- 2(\mathbf{J}_\xi\mathbf{P}_\xi + \mathbf{J}_\eta\mathbf{P}_\eta) + (\mathbf{P}_\xi^2 + \mathbf{P}_\eta^2)] = \bar{B}[J(J+1) - \Omega^2] + \bar{B}(\mathbf{P}_\xi^2 + \mathbf{P}_\eta^2) - \\ &- \bar{B}[(\mathbf{J}_\xi + i\mathbf{J}_\eta)(\mathbf{P}_\xi - i\mathbf{P}_\eta) + (\mathbf{J}_\xi - i\mathbf{J}_\eta)(\mathbf{P}_\xi + i\mathbf{P}_\eta)] \end{aligned} \quad (19)$$

where the first term in the last part is the energy of the symmetric top; the second is the expression (27) below. The last term yields (16) by (2) and (6).

Since $\mathbf{P}_\xi = \mathbf{L}_\xi + \mathbf{S}_\xi$, and $n' = n$, $v' = v$ and $\Omega' = \Omega \pm 1$ is such that $A' = A$ and $\Sigma' = \Sigma \pm 1$, substituting the form (1.1-26) of the eigenfunction into (17) yields by (1.2-17)

$$\begin{aligned} (\bar{B}P_\xi)(n, v, A, \Sigma; n, v, A, \Sigma \pm 1) &= \bar{B}_0 S_\xi(\Sigma; \Sigma \pm 1) \\ &= \frac{1}{2} \bar{B}_0 \sqrt{S(S+1) - \Sigma(\Sigma \pm 1)} \end{aligned} \quad (20)$$

and hence

$$\begin{aligned} H_{1a}^p(n, v, A, \Sigma; n, v, A, \Sigma \pm 1) \\ = \bar{B}_0 \sqrt{S(S+1) - \Sigma(\Sigma \pm 1)} \sqrt{J(J+1) - \Omega(\Omega \pm 1)} \end{aligned} \quad (21)$$

where \bar{B}_0 is the rotational constant at equilibrium inter-nuclear distance. Expression (21) describes the *interactions* among themselves of the components of the multiplet terms of *one and the same electronic state*, or, in other words, those perturbation-matrix elements by the help of which the *gradual transition from Hund's case a into case b* can be discussed in a quantum-mechanical way.

On the other hand, if $\Omega' = \Omega \pm 1$ is satisfied so that $A' = A \pm 1$ and $\Sigma' = \Sigma$, then expression (16) takes the form

$$\begin{aligned} H_{1a}^p(n, v, A, \Sigma; n', v', A \pm 1, \Sigma) &= 2(\bar{B}L_\xi)(n, v, A; n', v', A \pm 1) \times \\ &\times \sqrt{J(J+1) - \Omega(\Omega \pm 1)} \end{aligned} \quad (22)$$

and describes the interactions among the different electronic states, which—provided the terms are separated sufficiently—gives rise to A -type doubling. (Equation (22) should be complemented with (33) and (1.2-11) for a rigorous treatment.) It is these terms that will permit, among others, the discussion of perturbation among close-spaced terms in Chapter 4.

Case b. The matrix elements of the terms neglected in case *b* can be treated in exactly the same way as above, except that, because of the absence of

spin, operator \mathbf{L} replaces operator \mathbf{P} , and A replaces Ω everywhere. Accordingly, the matrix element corresponding to expression (16) is of the form

$$H_{bb}^p(n, v, A, N; n', v', A \pm 1, N) = 2(\bar{B}L_\xi)(n, v, A; n', v', A \pm 1) \times \\ \times \sqrt{N(N+1) - A(A \pm 1)} \quad (23)$$

where N is the rotational quantum number in case b .

Assuming that the orbital angular momentum \bar{L} is of a constant magnitude and that it uniformly precesses about the inter-nuclear axis (this is the assumption made in the *pure precession* hypothesis of van Vleck [211]) B and \mathbf{L} can be separated in (22) and (23), and e.g. (23) can be written as

$$H_{bb}^p(n, v, A, N; n', v', A \pm 1, N) \\ = \bar{B}_0 \sqrt{L(L+1) - A(A \pm 1)} \sqrt{N(N+1) - A(A \pm 1)} \quad (24)$$

By (24), the *gradual transition from Hund's case b to case d* can be treated quantum-mechanically.

Let us now examine the other neglected term in the wave equation and find the diagonal elements that are obtained from (1.1-27b).

Case a. Since (1.1-27b) does not contain the rotational coordinates, it follows from the orthogonality of the rotational part of the eigenfunction that only those matrix elements will differ from zero for which $\Delta J = 0$, $\Delta \Omega = 0$, $\Delta M = 0$. Since

$$\mathbf{P}_\xi^2 + \mathbf{P}_\eta^2 = (\mathbf{L}_\xi + \mathbf{S}_\xi)^2 + (\mathbf{L}_\eta + \mathbf{S}_\eta)^2 \\ = (\mathbf{L}_\xi^2 + \mathbf{L}_\eta^2) + (\mathbf{S}_\xi^2 + \mathbf{S}_\eta^2) + 2(\mathbf{L}_\xi \mathbf{S}_\xi + \mathbf{L}_\eta \mathbf{S}_\eta) \quad (25)$$

only the terms in the first two parentheses of the last expression give diagonal elements with respect to the further quantum numbers A and Σ ; hence, for these, $\Delta A = \Delta \Sigma = 0$. In addition, diagonal elements are also obtained from the second term of (1.1-27b). Forming the average of these terms over the electronic coordinates we obtain the detailed form of $\bar{U}(r)$ in (1.1-24b) as

$$\bar{U}(r) = \int \Phi_{n,A,\Sigma}^* \mathbf{H}_{2a} \Phi_{n,A,\Sigma} d\tau = \int \Phi_{n,A,\Sigma}^* \bar{B} \left[(\mathbf{L}_\xi^2 + \mathbf{L}_\eta^2) + (\mathbf{S}_\xi^2 + \mathbf{S}_\eta^2) \right] \Phi_{n,A,\Sigma} - \\ - r^2 \frac{\partial^2 \Phi_{n,A,\Sigma}}{\partial r^2} d\tau \quad (26)$$

For the calculation of the last term of (26) it is necessary to know the explicit form of Φ . Since this term is usually small in comparison with the preceding ones and as it depends only slightly on the inter-nuclear distance (so that it can be regarded as constant in components of the same multiplet) it can be incorporated into the expression of $W_0(r)$ or W_{el} in formulas (1.1-24b) or (1.1-32).

Thus the diagonal members contributing to the energy will be

$$H_{2a}^p(n, v, A, \Sigma; n, v, A, \Sigma) = \int R_{n,v}^* \bar{U}(r) R_{n,v} r^2 dr \\ = [\bar{B}(L_\xi^2 + L_\eta^2)]_{n,v,A}^{n,v,A} + \bar{B}_0[S(S+1) - \Sigma^2] \quad (27)$$

where we have made use of the formulas

$$\int R_{n,v}^* \bar{B} R_{n,v} r^2 dr = \bar{B}_0; (S_\xi^2 + S_\eta^2)_{\Sigma, \Sigma} = (S^2 - S_z^2)_{\Sigma, \Sigma} = S(S+1) - \Sigma^2 \quad (28)$$

since the vector \vec{S} is constant; furthermore

$$[\bar{B}(L_\xi^2 + L_\eta^2)]_{n,v,A}^{n,v,A} = \int \Phi_{n,A,\Sigma}^* R_{n,r}^* \frac{h^2}{8\pi^2 \mu r^2} (\mathbf{L}_\xi^2 + \mathbf{L}_\eta^2) \Phi_{n,A,\Sigma} R_{n,v} d\tau \quad (29)$$

Since (29) too gives identical values for the different components of the same multiplet, it is usually also incorporated in the expression of W_{el} . Thus in the solution of (1.1-24b), the taking into account of $\bar{U}(r)$ results in the appearance, within the parentheses, of the expression $S(S+1) - \Sigma^2$, in addition to $J(J+1) - \Omega^2$, in the last two terms of (1.1-41).

Case b. Similar considerations yield again (27) with the difference, however, that the second term containing the spin does not appear. Under the hypothesis of pure precession this result assumes a simple form:

$$H_{2b}^p(n, v, A; n, v, A) = \bar{B}_0 [L(L+1) - A^2] \quad (30)$$

In the discussion of the transition from case *b* to case *d*, this term cannot be incorporated into the value of W_{el} , since (30) no longer gives identical values for the terms interacting with each other. Thus, in the solution corresponding to case *b* of the wave equation (1.1-24b), (30) assumes the role of $\bar{U}(r)$ with the result that $L(L+1) - A^2$ appears in the last two terms of the solution (1.1-41) corresponding to case *b* (where now N and A stand instead of J and Ω).

The substitution of $\bar{U}(r)$ in (1.1-24b) does not, however, result merely in the appearance of the terms corresponding to (27) and (30), but also causes B_0 to be replaced by the quantity $B_v = B_e - \alpha_e(v + 1/2)$ (Dieke [42]).

For the non-diagonal matrix elements, formula (1.1-27b) yields according to van Vleck [214] the following expression for the cases $\Delta n = 0$ and $\Delta v = 0$:

$$H_{2a}^p(n, v, A, \Sigma; n', v', A, \Sigma) = \int R_{n,v}^* \left[P_{n,n'} + Q_{n,n'} + \left(-\frac{ih}{2\pi\mu} \right) \Omega_{n,n'} \mathbf{p}_r \right] R_{n',v'} r^2 dr \quad (31)$$

where

$$\begin{aligned} P_{n,n'}(r) &= \bar{B}(r) \int \Phi_{n,A,\Sigma}^* (\mathbf{P}_\xi^2 + \mathbf{P}_\eta^2) \Phi_{n',A,\Sigma} d\tau \\ Q_{n,n'}(r) &= -\bar{B}(r) r^2 \int \Phi_{n,A,\Sigma}^* \frac{\partial^2 \Phi_{n',A,\Sigma}}{\partial r^2} d\tau \\ \Omega_{n,n'}(r) &= \int \Phi_{n,A,\Sigma}^* \frac{\partial \Phi_{n',A,\Sigma}}{\partial r} d\tau; \quad \mathbf{p}_r = \frac{h}{2\pi i} \frac{\partial}{\partial r}; \quad \bar{B}(r) = \frac{h^2}{8\pi^2 \mu r^2} \end{aligned} \quad (32)$$

The first two terms of (31) are smaller by an order of magnitude than its last term.

The same applies to case *b*, except that, in the expression of $P_{n,n'}$, \mathbf{L}_ξ^2 and \mathbf{L}_η^2 will stand instead of \mathbf{P}_ξ^2 and \mathbf{P}_η^2 .

In addition to the above terms, some non-diagonal terms are obtained for which $\Delta A = -\Delta \Sigma = \pm 1$. The last term in (25), not taken into account so far, takes the following form when written out in detail:

$$H_{2a}^p(n, v, A, \Sigma; n', v', A \pm 1, \Sigma \mp 1) = 2(\bar{B}L_\xi)(n, v, A; n', v', A \pm 1) \times \\ \times \sqrt{S(S+1) - \Sigma(\Sigma \mp 1)} \quad (33)$$

where

$$(\bar{B}L_\xi)(n, v, A; n', v', A \pm 1) = \sum_A \int \bar{\Phi}_{n,A}^* R_{n,v}^* \bar{B}(r) \mathbf{L}_\xi \bar{\Phi}_{n',A \pm 1} R_{n',v'} r^2 dr d\tau \quad (34)$$

In the examination of *A*-type doubling and perturbations, (1.2-11b) is to be added to Formula (33).

In case *b*, Formula (33) has no equivalent since in this case there is no spin vector.

1.4. PERTURBATION MATRIX OF THE CENTRIFUGAL TERM

Let us now examine in more detail the last term of Equation (1.1-41) of the molecular energy. In order to gain insight into the physical meaning of this term we have to consider first the classical treatment of the rotating molecule. It is known that the kinetic energy of a rigid rotator spinning at the angular velocity ω is given by

$$W_{\text{kin}} = \frac{1}{2} \theta_e \omega^2 \quad (1)$$

where $\theta_e = \mu r_e^2$ is the moment of inertia of the rotator with respect to the axis of rotation. Since

$$\vec{R}_e = \theta_e \omega \quad (2)$$

where \vec{R}_e is the angular momentum, (1) can be written in the form

$$W_{\text{kin}} = \frac{\vec{R}_e^2}{2\theta_e} \quad (3)$$

If the rotating molecule is not a rigid rotator, then the inter-nuclear distance has to assume a value r_c such that the centrifugal force is cancelled by the restoring force $k(r_c - r_e)$ generated by the slight displacement $r_c - r_e$ from the equilibrium position r_e . The expression of the centrifugal force is

$$F_c = \mu r_c \omega^2 = \frac{\vec{R}^2}{\mu r_c^3} \quad (4)$$

where now $\vec{R} = \theta \omega = \mu r_c^2 \omega$. Equating the centrifugal force to the restoring force, we obtain for the change in the inter-nuclear distance

$$r_c - r_e = \frac{\vec{R}^2}{\mu r_c^3 k} \cong \frac{\vec{R}^2}{\mu r_e^3 k} \quad (5)$$

In the expression of the kinetic energy of rotation the new quantities \bar{R} and θ have to be written instead of \bar{R}_e and θ_e . In the case of a non-rigid rotator there arises a further term, the potential energy term $(1/2)k(r_c - r_e)^2$, so that the total energy of rotation is

$$W = \frac{\bar{R}^2}{2\mu r_e^2} + \frac{1}{2}k(r_c - r_e)^2 \quad (6)$$

Substituting r_c from Formula (5) and neglecting the higher powers of $(r_c - r_e)$, we obtain

$$W = \frac{\bar{R}^2}{2\mu r_e^2} - \frac{\bar{R}^4}{2\mu^2 r_e^6 k} + \dots \quad (7)$$

If the electron spin is coupled rigidly to the inter-nuclear axis and stays that way also under an increasing rotation (i.e. if *Hund's case a* prevails), then, by Fig. 1.4, $\bar{R}^2 = \bar{J}^2 - \bar{\Omega}^2$ and according to quantum mechanics we may write

$$\frac{h^2}{4\pi^2} [J(J+1) - \Omega^2]$$

and then, instead of (7),

$$\begin{aligned} W &= \frac{h^2}{8\pi^2 \mu r_e^2} [J(J+1) - \Omega^2] - \frac{h^4}{32\pi^4 \mu^2 r_e^6 k} [J(J+1) - \Omega^2]^2 + \dots \\ &= \bar{B}_e [J(J+1) - \Omega^2] - \bar{D}_e [J(J+1) - \Omega^2]^2 + \dots \end{aligned} \quad (8)$$

If (8) is compared with (1.1-41) it emerges that the latter expression reduces to the former if one neglects the electronic and vibrational energy. Nothing more could, of course, be expected of this simple consideration, since neither the electronic motion nor the vibration of the nuclei have been taken into consideration. It is, however, sufficient in that it shows that the last term of (1.1-41), the *centrifugal term*, arises from the change in the inter-nuclear distance due to the rotation of the molecule.

If the electron spin is totally uncoupled from the inter-nuclear axis by the increasing speed of rotation, then Ω is no longer defined and (8) ceases to hold. If, however, at the same time \bar{L} is still coupled to the inter-nuclear axis and stays so (in other words, if *Hund's case b* prevails), then by Fig. 1.5 we can write $\bar{R}^2 = \bar{N}^2 - \bar{A}^2$ and the centrifugal term becomes

$$H_b^e(A, N; A, N) = -\bar{D}[N(N+1) - A^2]^2 \quad (9)$$

This formula is, however, rigorously valid only when the electron spin is already fully coupled to the vector \bar{N} . To account for the gradual de-coupling from the inter-nuclear axis and for the coupling to the vector \bar{N} we have to use the perturbation method of quantum mechanics. To be able to do so, it is necessary to know the perturbation matrix. To set it up let us start

from (9) by expressing the vector \vec{N} in terms of the vector \vec{J} and \vec{S} . By Fig. 1.5

$$\vec{R}^2 = \vec{N}^2 - \vec{A}^2 = (\vec{J} - \vec{S})^2 - \vec{A}^2 \quad (10)$$

and by replacing the vectors by the relevant operators, we have

$$\begin{aligned} H^c = & -\bar{D}[\mathbf{N}^2 - \mathbf{A}^2]^2 = -\bar{D}[(\mathbf{J} - \mathbf{S})^2 - \mathbf{A}^2]^2 = -\bar{D}[\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{A}^2 - \\ & - 2(\mathbf{J}\mathbf{S})]^2 = -\bar{D}[\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{A}^2 - 2\mathbf{J}_z\mathbf{S}_z - 2(\mathbf{J}_x\mathbf{S}_x + \mathbf{J}_y\mathbf{S}_y)]^2 = -\bar{D}\{[\mathbf{J}^2 + \\ & + \mathbf{S}^2 - \mathbf{A}^2 - 2\mathbf{J}_z\mathbf{S}_z]^2 + 4(\mathbf{J}_x\mathbf{S}_x + \mathbf{J}_y\mathbf{S}_y)^2 - 4(\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{A}^2)(\mathbf{J}_x\mathbf{S}_x + \mathbf{J}_y\mathbf{S}_y) + \\ & + 4[\mathbf{J}_z\mathbf{S}_z(\mathbf{J}_x\mathbf{S}_x + \mathbf{J}_y\mathbf{S}_y) + (\mathbf{J}_x\mathbf{S}_x + \mathbf{J}_y\mathbf{S}_y)\mathbf{J}_z\mathbf{S}_z]\} \end{aligned} \quad (11)$$

Performing in detail the remainder of the calculation and using the relations (1.2-17), (1.3-15) and (1.3-6), the following matrix elements are obtained:

$$H_a^c(\Omega, \Sigma; \Omega, \Sigma) = -\bar{D}\{[f(J, \Omega) + f(S, \Sigma)]^2 + 2f(J, \Omega)f(S, \Sigma) + 2\Omega\Sigma\} \quad (12a)$$

$$\begin{aligned} H_a^c(\Omega, \Sigma; \Omega \pm 1, \Sigma \pm 1) = & -2\bar{D}[g_1(J, \Omega) + g_1(S, \Sigma) - 1] \times \\ & \times [g_1(J, \Omega)g_1(S, \Sigma)]^{1/2} \end{aligned} \quad (12b)$$

$$H_a^c(\Omega, \Sigma; \Omega \pm 2, \Sigma \pm 2) = -\bar{D}\{g_1(J, \Omega)g_1(S, \Sigma)g_2(J, \Omega)g_2(S, \Sigma)\}^{1/2} \quad (12c)$$

where

$$\begin{aligned} f(x, y) &= x(x+1) - y^2; \quad g_1(x, y) = x(x+1) - y(y \pm 1) \\ g_2(x, y) &= x(x+1) - (y \pm 1)(y \pm 2) \end{aligned} \quad (12d)$$

Clearly, the de-coupling of the spin modifies also the diagonal term corresponding to case *a*, so that a formula more complicated than (8) will hold. On the other hand, in the intermediate case between cases *a* and *b* the non-diagonal terms should also be taken into account by perturbation calculation. This aspect of the matter will be dealt with in the part concerned with term formulas of the next chapter.

One can discuss in a similar manner also the case in which the increasing rotation totally decouples also the vector \vec{L} from the inter-nuclear axis and couples it to the vector \vec{R} . Here \mathbf{A} is not defined either; nor is formula (9) valid. Thus in *Hund's case d* the vector \vec{R} itself is quantized and the centrifugal term assumes the form

$$H_d^c(R) = -\bar{D}R^2(R+1)^2 \quad (13)$$

If we want to follow the gradual de-coupling of vector \vec{L} , then, as in the former case, we have to express vector \vec{R} by vectors \vec{N} and \vec{L} ($\vec{R} = \vec{N} - \vec{L}$ by Fig. 1.7). Then (13) assumes the form

$$\begin{aligned} H^c = & -\bar{D}(\mathbf{R}^2)^2 = -\bar{D}[(\mathbf{N} - \mathbf{L})^2]^2 = -\bar{D}[\mathbf{N}^2 + \mathbf{L}^2 - 2(\mathbf{N}\mathbf{L})]^2 = -\bar{D}[\mathbf{N}^2 + \\ & + \mathbf{L}^2 - 2\mathbf{N}_z\mathbf{L}_z - 2(\mathbf{N}_x\mathbf{L}_x + \mathbf{N}_y\mathbf{L}_y)]^2 = -\bar{D}\{(\mathbf{N}^2 + \mathbf{L}^2 - 2\mathbf{N}_z\mathbf{L}_z)^2 + \\ & + 4(\mathbf{N}_x\mathbf{L}_x + \mathbf{N}_y\mathbf{L}_y)^2 - 4(\mathbf{N}^2 + \mathbf{L}^2)(\mathbf{N}_x\mathbf{L}_x + \mathbf{N}_y\mathbf{L}_y) + \\ & + 4[\mathbf{N}_z\mathbf{L}_z(\mathbf{N}_x\mathbf{L}_x + \mathbf{N}_y\mathbf{L}_y) + (\mathbf{N}_x\mathbf{L}_x + \mathbf{N}_y\mathbf{L}_y)\mathbf{N}_z\mathbf{L}_z]\} \end{aligned} \quad (14)$$

Detailed calculation yields the following matrix elements (cf. (12d)):

$$H_b(A, N; A, N) = -\bar{D} \{ [f(N, A) + f(L, A)]^2 + 2f(N, A)f(L, A) + 2.1^2 \} \quad (15a)$$

$$H_b(A, N; A \pm 1, N) = -2\bar{D} [g_1(N, A) + g_1(L, A) - 1] [g_1(N, A)g_1(L, A)]^{1/2} \quad (15b)$$

$$H_b(A, N; A \pm 2, N) = -\bar{D} \{g_1(N, A)g_1(L, A)g_2(N, A)g_2(L, A)\}^{1/2} \quad (15c)$$

In deriving the formulas valid for the intermediate case between cases *b* and *d*, the non-diagonal terms are also to be taken into consideration through perturbation calculation; this point will be discussed in the next chapter.

1.5. PERTURBATION CALCULATION

In order to derive formulas in agreement with experiment for the case of multiplet terms, the interactions dealt with in Sections 1.2, 1.3 and 1.4 have to be taken into account by perturbation calculations, using (1.1-41) as a starting point. Let us cover briefly all the details that are needed in the discussion to follow.

(i) Let us denote the operator of the separable wave equation by \mathbf{H}_0 , and the operator of the perturbation terms by \mathbf{H}^p ; then,

$$(\mathbf{H} - W'_i)\Psi'_i = 0 \quad (1)$$

must hold, where W'_i is the perturbed energy to be determined; Ψ'_i is the perturbed eigenfunction; and $\mathbf{H} = \mathbf{H}_0 + \mathbf{H}^p$. Since \mathbf{H}_0 is the operator of the separable wave equation,

$$(\mathbf{H}_0 - W_k)\Psi_k = 0 \quad (2)$$

where Ψ_k is the unperturbed eigenfunction and W_k is the unperturbed energy. Moreover

$$\int \Psi_k^* \mathbf{H}_0 \Psi_k d\tau = W_k; \quad \int \Psi_k^* \mathbf{H}_0 \Psi_l d\tau = 0, \quad k \neq l \quad (3)$$

The perturbed eigenfunctions can be written up as linear combinations of the unperturbed eigenfunctions:

$$\Psi'_i = \sum_k S_{ik} \Psi_k \quad (4)$$

Hence,

$$(\mathbf{H}_0 + \mathbf{H}^p - W'_i) \sum_k S_{ik} \Psi_k = 0 \quad (5)$$

Now multiplying from the left by Ψ'_i and integrating, we obtain

$$\sum_k S_{ik} \int \Psi'_i \mathbf{H}_0 \Psi_k d\tau + \sum_k S_{ik} \int \Psi'_i \mathbf{H}^p \Psi_k d\tau - \sum_k S_{ik} \int \Psi'_i W'_i \Psi_k d\tau = 0 \quad (6)$$

or, by (3),

$$S_{ii}(W_i - W'_i) + \sum_k S_{ik} H_{ik} = 0 \quad (7)$$

where

$$H_{ik} = \int \Psi_i^* \mathbf{H}^p \Psi_k d\tau \quad (8)$$

Formula (7), written out in detail, yields the following system of equations:

$$\begin{aligned} S_{i1}(W_1 - W'_i) + S_{i2}H_{12} &+ S_{i3}H_{13} + \dots + S_{in}H_{1n} = 0 \\ S_{i1}H_{21} &+ S_{i2}(W_2 - W'_i) + S_{i3}H_{23} + \dots + S_{in}H_{2n} = 0 \\ &\vdots \\ S_{i1}H_{n1} &+ \dots \dots \dots + S_{in}(W_n - W'_i) = 0 \end{aligned} \quad (9)$$

For this system to have a non-trivial solution, its determinant must disappear:

$$\begin{vmatrix} W_1 - W' & H_{12} & \dots & H_{1n} \\ H_{21} & W_2 - W' & \dots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & \dots & \dots & W_n - W' \end{vmatrix} = 0 \quad (10)$$

The solutions W'_1, \dots, W'_n of this secular equation provide the required perturbed energies. In the possession of these, one can calculate by formula (9) also the elements of the transformation matrix S .

(ii) The perturbation matrix is sometimes composed of the perturbation matrices of a number of interactions which differ by orders of magnitude. In such cases the above method of calculation would lead to a pointless complication of the final result; the most practical solution then is to select the greatest of the interaction terms and to perform on it the above operation; the remainder of the perturbations can then be taken into account as follows.

Let $\mathbf{H} = \mathbf{H}' + \bar{\mathbf{H}}^p$, where $\mathbf{H}' = \mathbf{H}_0 + \mathbf{H}^p$; \mathbf{H}_0 is the energy operator used at the first stage of the calculation; \mathbf{H}^p is the operator of the stronger perturbation, whereas $\bar{\mathbf{H}}^p$ is the weak-perturbation operator, to be taken into account at a later stage of the calculation. Then

$$(\mathbf{H}' + \bar{\mathbf{H}}^p - W'_i)\Psi''_i = 0 \quad (11)$$

holds, where $W''_i = W'_i + \Delta W'_i$ is the new perturbed energy and Ψ''_i is the new perturbed eigenfunction. If $\bar{\mathbf{H}}^p$ is small, then $\Delta W'_i$ will also be small and no great error will be committed if replacing Ψ''_i by Ψ'_i , the already perturbed eigenfunction of the operator \mathbf{H}' . Let $\Psi''_i \approx \Psi'_i$; then, since $(\mathbf{H}' - W'_i)\Psi'_i = 0$, we have in a good approximation

$$(\bar{\mathbf{H}}^p - \Delta W'_i)\Psi'_i = 0 \quad (12)$$

or

$$\Delta W'_i = \int \Psi'_i^* \bar{\mathbf{H}}^p \Psi'_i d\tau \quad (13)$$

Since, however, $\Psi'_i = \sum_k S_{ik} \Psi_k$, it follows that

$$\Delta W'_i = \int \sum_k S_{ik}^* \Psi_k^* \bar{\mathbf{H}}^p \sum_k S_{ik} \Psi_k d\tau \quad (14)$$

which, written out in detail, yields the following system:

$$\begin{aligned} \Delta W'_i = & S_{i1}^* (S_{i1} \bar{H}_{11}^p + S_{i2} \bar{H}_{12}^p + \dots \dots + S_{in} \bar{H}_{1n}^p) + \\ & + S_{i2}^* (S_{i1} \bar{H}_{21}^p + S_{i2} \bar{H}_{22}^p + \dots \dots + S_{in} \bar{H}_{2n}^p) + \\ & \vdots \\ & + S_{in}^* (S_{i1} \bar{H}_{n1}^p + S_{i2} \bar{H}_{n2}^p + \dots \dots + S_{in} \bar{H}_{nn}^p) \end{aligned} \quad (15)$$

Taken into account in this way, the weak interactions contribute additively to the strong perturbation already allowed for. Hence, they do not modify the formulas already established and the deviations stemming from them can be readily separated from the first perturbation. This is the case e.g. with the usually strong spin-orbit interaction, on the one hand, and the usually weaker spin-spin and rotation-spin interactions, or the interactions arising from the centrifugal term, on the other hand.

(iii) Where some of the multiplet molecular terms are perturbed by another multiplet term lying farther away, it proves necessary for assuring compatibility with experimental results to separate the perturbations among the components of the one multiplet term from the perturbations due to the other multiplet term. In such cases the following procedure can be applied.

Let $\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_0^p + \mathbf{H}^p$, where \mathbf{H}_0 is the energy operator corresponding to the separable wave equation, \mathbf{H}_0^p is the operator describing the perturbations among the components of the multiplet term under consideration, whereas \mathbf{H}^p is the perturbation operator of another, farther-lying multiplet term. Then

$$\begin{aligned} (\mathbf{H} - W'_i) \Psi''_i &= 0 \\ (\bar{\mathbf{H}}_0 - W'_i) \Psi'_i &= 0 \end{aligned} \quad (16)$$

where $\bar{\mathbf{H}}_0 = \mathbf{H}_0 + \mathbf{H}_0^p$, $\Psi'_i = \sum S_{ik} \Psi_k$ and $W'_i = \int \Psi_i'^* \bar{\mathbf{H}}_0 \Psi'_i d\tau$.

Furthermore,

$$(\bar{\mathbf{H}}_0 + \mathbf{H}^p - W'_i) \sum S'_{ik} \Psi'_k = 0 \quad (17)$$

by $\Psi''_i = \sum S'_{ik} \Psi'_k$. Multiplying (17) by $\Psi_i'^*$ and integrating, we obtain

$$S'_{ii} (W'_i - W''_i) + \sum S'_{ik} H'_{ik} = 0 \quad (18)$$

where

$$H'_{ik} = \int \Psi_i'^* \mathbf{H}^p \Psi'_k d\tau = \sum_m \sum_n S_{im}^* S_{kn} H_{mn}^p \quad (19)$$

and

$$H_{mn}^p = \int \Psi_m^* \mathbf{H}^p \Psi_n d\tau \quad (20)$$

Now, since \mathbf{H}^p is the operator of the interaction between the two multiplet terms, we see that if the multiplicity of one term is s , and that of the other is r , obviously only those elements of H_{mn}^p will differ from zero for which $0 < m \leq s$ and $s < n \leq r + s$. Hence, (19) assumes the form

$$\begin{aligned} H'_{lk} = & (S_{l1}^* H_{1,s+1}^p + S_{l2}^* H_{2,s+1}^p + \dots \dots \dots + S_{ls}^* H_{s,s+1}^p) S_{k,s+1} + \\ & + (S_{l1}^* H_{1,s+2}^p + S_{l2}^* H_{2,s+2}^p + \dots \dots \dots + S_{ls}^* H_{s,s+2}^p) S_{k,s+2} + \\ & \vdots \\ & + (S_{l1}^* H_{1,s+r}^p + S_{l2}^* H_{2,s+r}^p + \dots \dots \dots + S_{ls}^* H_{s,s+r}^p) S_{k,s+r} \end{aligned} \quad (21)$$

Furthermore

$$H'_{lk} = 0 \begin{cases} \text{if } l \leq s \text{ and } k \leq s; \text{ then } H_{mn}^p = 0 \text{ (} n < s \text{)} \\ \text{if } s < l \leq s + r \text{ and } s < k \leq s + r; \text{ then } H_{mn}^p = 0 \text{ (} m > s \text{)} \end{cases} \quad (22)$$

Accordingly, the condition for the solubility of (18) is of the form

$$\begin{vmatrix} W'_1 - W'' & 0 & \dots & 0 & H'_{1,s+1} & \dots & H'_{1,s+r} \\ 0 & W'_2 - W'' & \dots & 0 & H'_{2,s+1} & \dots & \vdots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & W'_s - W'' & H'_{s,s+1} & \dots & H'_{s,s+r} \\ H'_{s+1,1} & \dots & H'_{s+1,s} & W'_{s+1} - W'' & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & 0 & W'_{s+2} - W'' & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ H'_{s+r,1} & \dots & H'_{s+r,s} & 0 & 0 & \dots & W'_{s+r} - W'' \end{vmatrix} = 0 \quad (23)$$

where the multiplet formulas containing the perturbation \mathbf{H}_0 are found along the diagonal (the experimentalist can regard *this* as the unperturbed term); the off-diagonal terms (which express the perturbation among the respective components of the two distinct terms) can be calculated from (21).

In order to calculate the perturbation energies W'' , Equation (23) has to be solved. There are two ways of doing this.

(i) If the multiplet spacing is great as compared with the spacing of the components, the perturbation calculation for non-degenerate systems yields for the perturbed energies

$$W''_i = W'_i + \frac{\sum_k |H'_{ik}|^2}{\nu} \quad (24)$$

where $i \leq s$ entails $k = s + 1, \dots, s + r$; $s < i \leq s + r$ entails $k = 1, \dots, s$; and ν means the multiplet spacing, considered equal for all components.

(ii) If the multiplet spacing is not wider, or indeed narrower, than the component spacing (such a case is encountered e.g. when two multiplet components cross each other as plotted against the rotational quantum number) then, neglecting the interactions among the farther-lying terms and taking into account only the interaction between the two components close to each other, the following simple secular equation can be written up:

$$\begin{vmatrix} W'_i - W'' & H'_{ik} \\ H'_{ki} & W'_k - W'' \end{vmatrix} = 0 \quad (25)$$

The solution of this equation is

$$W''_{i,k} = \frac{W'_i + W'_k}{2} \pm \sqrt{\left(\frac{W'_i - W'_k}{2}\right)^2 + |H'_{ik}|^2} \quad (26)$$

which often proves to be a sufficient approximation in the neighbourhood of the crossing point.

MULTIPLY TERM FORMULAS

As mentioned above, most of the observed molecular spectra exhibit a multiplet structure. The multiplying of a spectral line is due to the multiplying of the terms involved in the transition, giving rise to the line in question. These multiplet terms are not accounted for by expression (1.1-41) obtained from the separable wave equation. To obtain multiplet term formulas in agreement with the experimental findings, the interactions discussed in the previous chapter have to be taken into consideration.

The multiplying of the terms can be due to two reasons: (i) the different orientations of the resultant spin momentum \vec{S} of the molecule involve different energies; and (ii) the different orientations of the resultant orbital angular momentum \vec{L} of the molecule also entail different energy levels. The first case can be termed the case of S , or *spin multiplets*, and the second the L -multiplets. In the first case, according as the spin momentum is coupled to the inter-nuclear axis or to the axis of rotation, we refer to *Hund's case a* or *b*; in the second case, according as the orbital angular momentum is coupled to the inter-nuclear axis or to the axis of rotation, we speak of *Hund's case a*, *b* or *d*. (If the spin is neglected, there is no difference between *Hund's cases a* and *b*.) The energy values corresponding to the above limiting cases can be readily obtained by complementing Formula (1.1-41) with the diagonal terms of the interactions discussed in the previous chapter using formula (1.1-41) in case *a*, introducing N and A instead of J and Ω in case *b* and R and zero instead of J and Ω in case *d*. Even the energy expressions obtained in this way will, however, seldom lead to values in agreement with experiment; this is understandable inasmuch as these limiting cases practically mean neglecting all interactions, with the exception of a few. In the actual molecule, however, all interactions are operative to a greater or lesser extent. Results compatible with experimental findings can be obtained, however, if these energy values are used initially, i.e. those of the unperturbed system, and the non-diagonal matrix elements of all interactions are taken into consideration by perturbation calculation. In this way we can obtain energies or term values intermediate between *Hund's* limiting cases. These intermediate values are capable of describing the gradual transition from one limiting case to another. Accordingly, first we shall deal with spin multiplets and discuss the case of L -multiplets later on.

2.1. SPIN MULTIPLETS AND Λ -TYPE DOUBLING

In the following discussion, the spin-multiplet term formulas of the rotational fine structure will be derived for intermediate cases between *Hund's* cases a and b , up to and including septet terms. In doing so one can start either from *Hund's* case a , or from case b . In the present treatment we shall start from case a and proceed up to the quartet terms; the intermediate energy expressions will be derived taking into account the spin-orbit interaction and, by formula (1.5-10), the terms neglected on the separation of the wave equation. Knowing these energy expressions, the elements of the transformation matrix will be determined by (1.5-9); then, in possession of these latter, the intermediate-case forms for the centrifugal correction, spin-spin, and rotation-spin interactions will be written up according to (1.5-15). These latter terms will be found to occur as additive correction complementing the usual term formulas.

In the case of terms of multiplicities higher than quartets this procedure runs into serious mathematical difficulties. It has so far yielded only formulas that give a good approximation only in the neighbourhood of case b . For this reason we shall, starting from case b , derive an approximate energy formula, valid in the neighbourhood of case b , from (1.5-10) by means of the case b perturbation-matrix elements of the spin-orbit interaction. Subsequently, we shall take into account the centrifugal correction, the spin-spin interaction and the rotation-spin interaction in their case b forms.

Parallel to the gradual de-coupling of the spin momentum from the internuclear axis and its coupling to the axis of rotation we can observe also the de-coupling of the orbital angular momentum; or, expressing it in quantum-mechanical terms, the perturbation is not restricted to the individual multiplet components but extends also to terms lying relatively far from one another. As a consequence, we have to deal with the phenomenon of Λ -type doubling, as well as the multiplet term formulas.

2.1.1. *Energies and Perturbation-Matrix Elements in the Limiting Cases*

To facilitate calculations, we shall now list all the energy expressions and perturbation matrix elements which are found scattered throughout the previous chapter; we shall express them all in term values (with all constants divided by hc , so that all the flags above the symbols can be omitted, e.g.: $B = \bar{B}/hc$, $D = \bar{D}/hc$ etc.).

Case a

$$T_{\Omega}(J) = v_0 + A\Lambda\Sigma + B[J(J+1) - \Omega^2 + S(S+1) - \Sigma^2] \quad (1a)$$

$$H_a^p(A, \Sigma; A, \Sigma \pm 1) = B[S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2} [J(J+1) - \Omega(\Omega \pm 1)]^{1/2} \quad (1b)$$

$$H_a^2(A, \Sigma; A \pm 1, \Sigma) = 2(BL_{\epsilon})(A; A \pm 1) [J(J+1) - \Omega(\Omega \pm 1)]^{1/2} \quad (1c)$$

$$H_a^{p+so}(A, \Sigma; A \pm 1, \Sigma \mp 1) = H_a^p + H_a^{so} \\ = (AL_\xi + 2BL_\xi)(A, A \pm 1)[S(S+1) - \Sigma(\Sigma \mp 1)]^{1/2} \quad (1d)$$

$$H_a^c(A, \Sigma; A, \Sigma) = -D \{ [J(J+1) - \Omega^2 + S(S+1) - \Sigma^2]^2 + \\ + 2[J(J+1) - \Omega^2][S(S+1) - \Sigma^2] + 2\Omega\Sigma \} \quad (2a)$$

$$H_a^c(A, \Sigma; A, \Sigma \pm 1) = -2D[J(J+1) - \Omega(\Omega \pm 1) + S(S+1) - \\ - \Sigma(\Sigma \pm 1) - 1][S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2}[J(J+1) - \Omega(\Omega \pm 1)]^{1/2} \quad (2b)$$

$$H_a^c(A, \Sigma; A, \Sigma \pm 2) = -D \{ [S(S+1) - \Sigma(\Sigma \pm 1)][S(S+1) - \\ - (\Sigma \pm 1)(\Sigma \pm 2)][J(J+1) - \Omega(\Omega \pm 1)][J(J+1) - (\Omega \pm 1)(\Omega \pm 2)] \}^{1/2} \quad (2c)$$

$$H_a^{ss}(A, \Sigma; A, \Sigma) = \varepsilon[3\Sigma^2 - S(S+1)] \quad (3a)$$

$$H_a^{ss}(A = +1, \Sigma = -1; A' = -1; \Sigma' = +1) = 1/2 \alpha S(S+1) \quad (3b)$$

$$H_a^{sr}(A, \Sigma; A, \Sigma) = \gamma[\Sigma^2 - S(S+1)] \quad (4a)$$

$$H_a^{sr}(A, \Sigma; A, \Sigma \pm 1) = -\frac{\gamma}{2}[S(S+1) - \Sigma(\Sigma \pm 1)]^{1/2}[J(J+1) - \\ - \Omega(\Omega \pm 1)]^{1/2} \quad (4b)$$

Here, (1a) has been written up on the basis of (1.1-41), (1.2-11a) and (1.3-27); in it, v_0 means the part of the term value that is independent of J , Σ and S ; (1b) is based on (1.3-21); (1c) on (1.3-22); (1d) on (1.2-11b) and (1.3-33); (2a), (2b) and (2c) are derived from (1.4-12); (3a) and (3b) are derived from (1.2-18a), (1.2-18c); and finally, (4a) and (4b) are derived from (1.2-27a) and (1.2-27b).

Case b

$$T_A(N) = v_0 + B[N(N+1) - A^2] + \\ + A A^2 \frac{J(J+1) - N(N+1) - S(S+1)}{2N(N+1)} \quad (5a)$$

$$H_b^{so}(A, N; A, N+1) \\ = A A \{ [(N+1)^2 - A^2][(J+N+1)(J+N+2) - S(S+1)] \}^{1/2} \times \\ \times \frac{[S(S+1) - (J-N)(J-N-1)]^{1/2}}{2(N+1)[(2N+1)(2N+3)]^{1/2}} \quad (5b)$$

$$H_b^e(A, N; A, N) = -D[N(N+1) - A^2]^2 \quad (6)$$

$$H_b^{ss}(A, N; A, N) = -2\varepsilon \frac{{}^3/{}_4 C(C+1) - N(N+1)S(S+1)}{(2N-1)(2N+3)} \times \\ \times \left[1 - \frac{3A^2}{N(N+1)} \right] \quad (7a)$$

$$H_b^{ss}(A = +1, N; A' = -1, N) = \alpha \frac{{}^3/{}_4 C(C+1) - N(N+1)S(S+1)}{(2N-1)(2N+3)} \quad (7b)$$

$$C = J(J+1) - N(N+1) - S(S+1) \quad (7c)$$

$$H_b^{sr}(A, N; A, N) = \frac{\gamma}{2} [J(J+1) - N(N+1) - S(S+1)] \left[1 - \frac{A^2}{N(N+1)} \right] \quad (8)$$

Here, (5a) is derived from (1.1-41) and (1.2-33a); (5b) from (1.2-33b); (6) from (1.4-9); (7a) and (7b) from (1.2-41); and (8) from (1.2-47).

Hund's limiting cases can be characterized by well-defined values of certain parameters. For the intermediate cases between *Hund's* cases *a* and *b*, the ratio $Y = A/B$ (A is the coupling constant of the spin-orbit interaction and B is the rotational constant) can be chosen as such a parameter. *Hund's* case *a* is characterized, in terms of this ratio, by $Y \gg J(J+1)$; in case *b*, $Y \ll N(N+1)$.

In view of the foregoing considerations, in *Hund's* case *a* the term formula valid for terms of any type and multiplicity (i.e. for any value of A and Σ) is the following:

$$F_a(A, S, Y \gg J(J+1)) = \nu_0 + AA\Sigma + B[J(J+1) - \Omega^2 + \\ + S(S+1) - \Sigma^2] + H_a^e(A, S) + H_a^{ss}(A, S) + H_a^{sr}(A, S) \quad (9)$$

where the explicit values of the last three terms are to be taken from (2a), (3a,b) and (4a).

For *Hund's* case *b*, the following formula holds for terms of any type and multiplicity:

$$F_b(A, S, Y \ll N(N+1)) = \nu_0 + B[N(N+1) - A^2] + \\ + AA^2 \frac{J(J+1) - N(N+1) - S(S+1)}{2N(N+1)} + H_b^e(A) + H_b^{ss}(A, S) + H_b^{sr}(A, S) \quad (10)$$

where the last three terms are to be taken from Formulas (6), (7a,b) and (8). In the case of pure precession it is usual to write up separately the term $B[L(L+1) - A^2]$ commonly included in ν_0 .

As has been mentioned previously, these expressions rarely give values compatible with experiment. Formulas that are less general with respect to the quantum number S , i.e. limited to terms of a given multiplicity, but valid for any value of the parameter Y , are much more useful. The tabulation below illustrates this point.

Case a [$Y \gg J(J+1)$] S	Intermediate case between a and b $+\infty > Y > 0$	Case b [$Y \ll N(N+1)$] S
0	singlet cases a and b coincide	0
$1/2$	doublet \longleftrightarrow	$1/2$
1	triplet \longleftrightarrow	1
$3/2$	quartet \longleftrightarrow	$3/2$
2	quintet \longleftrightarrow	2
$5/2$	sextet \longleftrightarrow	$5/2$
3	septet \longleftrightarrow	3

The term formulas in the first and third columns of the above table are (9) and (10). In the following we shall write up for the cases indicated by arrows formulas of the type $F(\Lambda, S = \text{const.}, Y)$, where S is fixed but Λ and Y can assume any value, for both the terms and the Λ -type splittings.

2.1.2. Singlet Terms

(a) Term Formulas. For the sake of completeness, singlet terms will also be discussed here, although for them there is no intermediate case, since *Hund's* cases a and b coincide. Therefore, the singlet-term formula can be obtained either from (2.1.1-9) by putting $S = \Sigma = 0$, or from (2.1.1-10) by putting $S = 0$ and $J = N$. Both yield the result

$$F(J) = \nu_0 + B[J(J+1) - \Lambda^2] - D[J(J+1) - \Lambda^2]^2 \quad (1)$$

In the case of $\Lambda = 0$, i.e. for $^1\Sigma$ terms, perturbation by energetically far-away terms does not essentially modify the term formula. The perturbations by the other $^1\Sigma$ terms do modify somewhat the value of ν_0 but do not alter the form of the formula and do not affect the dependence on the rotational quantum number.

Perturbations by the $^1\Pi$ terms affect, as can readily be shown making use of (2.1.1-1c), the value of the rotational constant in the following way (Mulliken and Christy [159]):

$$B'_\Sigma = B_\Sigma + \sum_i \frac{8|\eta(\Sigma, \Pi_i)|^2}{\nu(\Sigma, \Pi_i)} \quad (2)$$

where $|\eta(\Sigma, II_i)| = |(BL_\xi)(^1\Sigma, ^1II_i)|$ and $\nu(\Sigma, II_i)$ is the spacing of the two terms, whose dependence on the rotational quantum number is assumed to be negligible. The summation is to be extended over all vibrational levels of all perturbing states 1II_i .

Perturbations of terms of higher multiplicity can be discussed by considering Formula (1.2-9b) of the spin-orbit interaction. This topic will be discussed in detail in Chapter 4; it is sufficient to state here that these perturbations also affect only the value of ν_0 , and rather slightly at that.

If among the terms 1II_i there is one so close to the term $^1\Sigma$ that the effect of all the other terms can be neglected, but the change of $\nu(^1\Sigma, ^1II_i)$ with the rotational quantum number cannot, then

$$\nu(^1\Sigma, ^1II_i) \approx \nu + (B_\Sigma - B_{II})N(N+1) \quad (3)$$

where ν means the spacing of the vibrational levels. A series expansion then yields

$$\frac{1}{\nu(^1\Sigma, ^1II_i)} \sim \frac{1}{\nu} - \frac{(B_\Sigma - B_{II})N(N+1)}{\nu^2} \quad (4)$$

Substitution into the term formula gives

$$\overline{F(N)} = \nu_0 + \overline{B}_\Sigma N(N+1) - \overline{D}_\Sigma N^2(N+1)^2 \quad (5)$$

where

$$\overline{B}_\Sigma = B_\Sigma + \frac{8\eta^2}{\nu}; \quad \overline{D}_\Sigma = D_\Sigma + \frac{8\eta^2(B_\Sigma - B_{II})}{\nu^2} \quad (6)$$

Hence, in the case of terms $^1\Sigma$, perturbation by the neighbouring terms does not affect the dependence on the rotational quantum number. This is precisely the reason that the perturbation remains unobserved in most cases; it is formula (5) that appears as the unperturbed form of the term $^1\Sigma$ to the experimental spectroscopist.

(b) Λ -Type Doubling. If $A > 0$, then the term values are twofold degenerate and this degeneracy is split up by increasing rotation. As mentioned above, this phenomenon can be regarded as the beginning of the L -de-coupling process, since in the model treatment it corresponds to the incipient de-coupling of the resultant orbital angular momentum vector of the electrons from the inter-nuclear axis and to its incipient coupling to the rotational axis (if the latter coupling were complete we would speak of *Hund's case d*). In the quantum-mechanical treatment, this phenomenon appears in the form of a gradually intensifying asymmetric perturbation by the neighbouring terms, first of all $^1\Sigma$, which then leads to the splitting of the term values.

In the case of the 1II terms (2.1.1-1c) yields, according to van Vleck, [211] the term formulas

$$\begin{aligned} F_c(J) &= \nu'_0 + B_c J(J+1) - DJ^2(J+1)^2 \\ F_d(J) &= \nu'_0 + B_d J(J+1) - DJ^2(J+1)^2 \end{aligned} \quad (7)$$

where

$$\nu'_0 = \nu_0 - BA^2 - DA^4 - 8 \sum_i \frac{|\eta(II; A_i)|^2}{\nu(II; A_i)} \quad (8)$$

$$B_c = B + 2A^2D + 4 \sum_i \frac{|\eta(II; \Delta_i)|^2}{v(II; \Delta_i)} + 8 \sum_i \frac{|\eta(II; \Sigma_i^+)|^2}{v(II; \Sigma_i^+)}$$

$$B_d = B + 2A^2D + 4 \sum_i \frac{|\eta(II; \Delta_i)|^2}{v(II; \Delta_i)} + 8 \sum_i \frac{|\eta(II; \Sigma_i^-)|^2}{v(II; \Sigma_i^-)} \quad (9)$$

The summation is to be extended over all vibrational states of all terms of similar type.

From Formulas (7) and (9) we obtain for the Λ -type splitting

$$\Delta F_{cd}(J) = (B_c - B_d)J(J + 1) \quad (10)$$

It is apparent that the perturbation by the terms ${}^1\Lambda$ gives rise to only a slight modification of v_0 and B in the term formula, but does not cause splitting. The case is similar to the perturbations of terms ${}^3\Sigma$, ${}^3\Pi$ and ${}^3\Lambda$, except that here only v_0 is slightly modified. These perturbations can also be treated by using form (1.2-9b) of the spin-orbit interaction. It is very seldom that these perturbations can be detected. Formula (10) has been applied many times to experimental results: among these applications, let us recall here—following Kovács [100]—the values observed by Heimer [69] of the difference $B_c - B_d = \Delta F_{cd}(J)/J(J + 1)$ for the splitting at the $v=0$ level of the term ${}^1\Pi$ in the transition ${}^1\Sigma^+ - {}^1\Pi$ in the red part of the spectrum of BiH (cf. also 4.4.1-7). By Fig. 2.1 the observed value

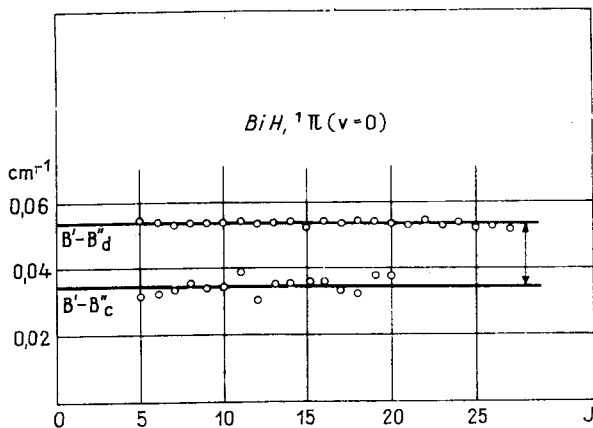


Fig. 2.1 Λ -type doubling observed at the $v = 0$ level of ${}^1\Pi$ in the BiH molecule, according to Kovács [100]. The differences between the rotational constant B of the upper ${}^1\Sigma^*$ state and the rotational constants B_c and B_d , respectively, of the Λ -type doublet components of the lower ${}^1\Pi$ state are plotted vs. the rotational quantum number. The distance between the two straight lines (indicated by an arrow) is the difference $B_c - B_d$, equal to 0.019 cm^{-1} .

of $B_c - B_d$ is 0.019 cm^{-1} , whereas the value calculated by formulas (9) and (13) is 0.022 cm^{-1} for $L = 1$, which can be regarded as a good agreement, considering that the condition of pure precession is rarely satisfied in reality (see below).

In the case of 1A terms it is only the second-order approximation that shows up any splitting; even this is, however, of a lower order of magnitude than in the previous case. It is, according to Kronig [135] and van Vleck [212], described by

$$\Delta F_{cd}(J) = d(J - 1)J(J + 1)(J + 2) \quad (11)$$

where

$$d = \sum_{i,k} \frac{32 |\eta(A; \Pi_i)|^2 |\eta(\Pi_i; \Sigma_k)|^2}{v^2(A; \Pi_i) v^2(A; \Sigma_k)} \quad (12)$$

If the resultant orbital angular momentum \vec{L} of the electrons precesses uniformly about the internuclear axis, then there is a well-defined quantum number corresponding to it. If in such a case there is only one dominant perturbing term, and both this term and the perturbed one belong to the same L value (this is the case of *pure precession* according to van Vleck [211]), then the summation can be neglected and

$$|\eta(A; A \pm 1)| = |BL_c(A; A \pm 1)| = \frac{1}{2}B[L(L + 1) - A(A \pm 1)]^{1/2} \quad (13)$$

Thus if the spacing of the term in question is known, the order of magnitude of the splitting constant can be estimated from theory; indeed, in many cases it can be calculated rather accurately (see the experimental example given above).

2.1.3. Doublet Terms

(a) General Theory of Spin Splitting. In the case of doublet terms the perturbation theory by (1.5-10) yields for the intermediate case between *Hund's* cases *a* and *b* the second-order secular equation as

$$\begin{vmatrix} \Omega = A - \frac{1}{2} & T_1^0 - T & H_{12}^0 \\ \Omega = A + \frac{1}{2} & H_{21}^0 & T_2^0 - T \end{vmatrix} = 0 \quad (1)$$

where by (2.1.1-1a, b)

$$\begin{aligned} T_1^0 &= v_0 - \frac{1}{2}A + B[(J + \frac{1}{2})^2 - A(A - 1)] \\ T_2^0 &= v_0 + \frac{1}{2}A + B[(J + \frac{1}{2})^2 - A(A + 1)] \\ H_{12}^0 &= H_{21}^0 = B\sqrt{(J + \frac{1}{2})^2 - A^2} \end{aligned} \quad (2)$$

The solution of (1) is

$$\begin{Bmatrix} T_1 \\ T_2 \end{Bmatrix} = \frac{T_1^0 + T_2^0}{2} \mp \sqrt{\left(\frac{T_2^0 - T_1^0}{2}\right)^2 + |H_{12}^0|^2} \quad (3)$$

Owing to the opposite symmetry of the wave functions, in the case of $A > 0$, two identical secular determinants are obtained; the energy and term values will therefore be twofold degenerate. The writing out of (3) in detail yields

$$\begin{aligned} T_{J-1/2}(J) &= v_0 + B[(J + 1/2)^2 - A^2 - 1/2 \sqrt{A^2 Y(Y - 4) + 4(J + 1/2)^2}] \\ T_{J+1/2}(J) &= v_0 + B[(J + 1/2)^2 - A^2 + 1/2 \sqrt{A^2 Y(Y - 4) + 4(J + 1/2)^2}] \end{aligned} \quad (4)$$

where $Y = A/B$. The term is called normal if $A > 0$, and inverted if $A < 0$. Formula (4) is valid for all values of Y intermediate between *Hund's* cases a and b ; for $Y \gg J(J + 1)$ it reduces to the case a formulas given in (2); for $Y \ll J(J + 1)$ it can be obtained in its case b form from (2.1.1-5a). Expression (4) was first derived by Hill and van Vleck [77] from case b .

Making use of (4), the elements of the transformation matrix can also be formed from (1.5-9) as

$$\begin{aligned} S_{A-1/2, J-1/2} &= \sqrt{\frac{2(J - A + 1/2)(J + A + 1/2)}{C^-(J)}}; & S_{A+1/2, J-1/2} &= -\frac{u^-(J)}{\sqrt{2C^-(J)}} \\ S_{A-1/2, J+1/2} &= \sqrt{\frac{2(J - A + 1/2)(J + A + 1/2)}{C^+(J)}}; & S_{A+1/2, J+1/2} &= \frac{u^+(J)}{\sqrt{2C^+(J)}} \end{aligned} \quad (5)$$

where

$$\begin{aligned} u^\pm(J) &= [A^2 Y(Y - 4) + 4(J + 1/2)^2]^{1/2} \pm A(Y - 2) \\ C^\pm(J) &= 1/2\{u^\pm(J)^2 + 4[(J + 1/2)^2 - A^2]\} \end{aligned} \quad (6)$$

In more rigorous investigations, however, the term formula (4) given above should be complemented with certain correction terms. One of these corrections is due to the fact that, owing to the centrifugal force in action, an increased rotation entails an increase in the inter-nuclear distance and a decrease in the rotational constant. This effect can be described in *Hund's* case b by the following simple formula derived from (2.1.1-6):

$$H_b^c = -D[N(N + 1) - A^2]^2 \quad (7)$$

In many cases (7) proves adequate; however, when the term belongs to case a for low values of the rotational quantum number and to case b for

the higher values, then it is necessary to use an intermediate form between cases *a* and *b*. To obtain this form, let us start from expressions (2.1.1-2a, b) derived for the term 2H by Almy and Horsfall [9] in a way different from the one which we shall follow here. In a general form, for any type of doublet terms, we obtain by the above considerations

$$H_a^c = \left\| \begin{array}{cc} -D[(J_A^2 + A)^2 + J_A^2] & -2DJ_A^3 \\ -2DJ_A^3 & -D[(J_A^2 - A)^2 + J_A^2] \end{array} \right\| \begin{array}{l} \Omega = A - 1/2 \\ \Omega = A + 1/2 \end{array} \quad (8)$$

where

$$J_A^2 = (J + 1/2)^2 - A^2 \quad (9)$$

Almy and Horsfall [9] added (8) to the elements of (1) and solved the modified secular determinant so obtained. This is undoubtedly a correct procedure but it complicates the structure of expression (4), and leads to an involved expression, which becomes even more complicated for higher multiplets. Moreover, the entire procedure has to be reiterated from the beginning in case further corrections are to be added, and it is difficult to determine from the final formulas the effects the individual corrections have had. These pitfalls can be avoided by adopting the procedure described in Section 1.5 and by using the transformation-matrix elements of (5) and the elements of (8), in which case the correction terms are obtained in additive form without any modification of (4). Thus by (1.5-15) the explicit expression for the intermediate form of the centrifugal term between cases *a* and *b* becomes

$$H_N^c(J) = -D\{J_A^2(J_A^2 + 1) + A^2 + 2AJ_A^2(S_{A-1/2,N}^2 - S_{A+1/2,N}^2) - 4S_{A+1/2,N}S_{A-1/2,N}J_A^3\} \quad (10)$$

When substituting $J - 1/2$ or $J + 1/2$ for N , expression (10) is to be added to (4). Formula (10) reduces to (7) in *Hund's* case *b* ($Y = 0$), whereas in case *a* ($Y \rightarrow \infty$) it yields the diagonal elements of (8).

A further correction becomes necessary to account for the interaction between rotation and spin. In the doublet case this correction assumes by (2.1.1-8) for *Hund's* case *b* the form

$$H_b^{sr} = 1/2 \gamma [J(J + 1) - N(N + 1) - 3/4] \left[1 - \frac{A^2}{N(N + 1)} \right] \quad (11)$$

For establishing the intermediate form of this interaction between cases *a* and *b* we need the case *a* form of Formula (11). By (2.1.1-4a, b), this assumes for doublet terms the form

$$H_a^{sr} = \left\| \begin{array}{cc} -\frac{\gamma}{2} & -\frac{\gamma}{2} J_A \\ -\frac{\gamma}{2} J_A & -\frac{\gamma}{2} \end{array} \right\| \begin{array}{l} \Omega = A - 1/2 \\ \Omega = A + 1/2 \end{array} \quad (12)$$

Using (5) and (1.5-15) we obtain for the intermediate case in a manner similar to (10)

$$H_N^{sr}(J) = \frac{\gamma}{2} [2S_{A+1/2, N} S_{A-1/2, N} J_A - 1] \quad (13)$$

After the substitution of $J - 1/2$, and $J + 1/2$ for N , Formula (13) is to be added to (4). Formula (13) reduces to (11) in *Hund's case b* ($Y = 0$); in *Hund's case a* ($Y \rightarrow \infty$) it yields the diagonal elements of (12).

In definitive, the complete term formulas for doublet terms in the intermediate case between *Hund's cases a* and *b* will be

$$F_N(J) = T_N(J) + H_N^c(J) + H_N^{sr}(J) \quad (14)$$

where $N = J - 1/2, J + 1/2$.

${}^2\Sigma$ Terms. The formula valid for ${}^2\Sigma$ terms can be obtained from (14) by putting $\Lambda = 0$ and $Y = 0$. Then

$$\begin{aligned} F_{J-1/2}(N) &= F_1(N) = v_0 + B_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 + 1/2 \gamma N \\ F_{J+1/2}(N) &= F_2(N) = v_0 + B_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 - 1/2 \gamma(N+1) \end{aligned} \quad (15)$$

By (15) we obtain for the doublet splitting

$$\Delta F_{12}(N) = \gamma(N + 1/2) \quad (16)$$

Many applications of the above formula can be found in Mulliken and Christy [159]. Of these, we have reproduced here the splitting of one of the ${}^2\Sigma$ states of CdH at the level $v = 0$ (Fig. 2.2). In some cases, however, a deviation from (16) was found, the reason of which shall be discussed subsequently.

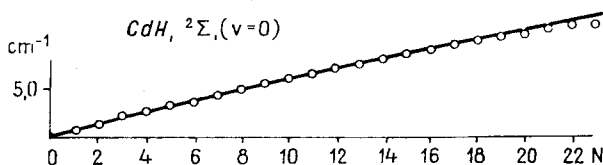


Fig. 2.2 Doublet splitting at the ${}^2\Sigma$, $v = 0$ level of CdH, according to Mulliken and Christy [159]; $\gamma = 0.59 \text{ cm}^{-1}$.

On examining the effect of perturbation by farther-lying terms upon the term formula it is found that the perturbation by the terms ${}^4\Sigma$, ${}^4\Pi$ and by other ${}^2\Sigma$ terms, transferred by the spin-orbit interaction, affects only v_0 , so that there is no change in the doublet splitting. Let us examine more closely the influence upon the term

formula of perturbation by the 2H terms; (15) then modifies, according to van Vleck [211], to read

$$\begin{aligned} F'_1(N) &= v'_0 + B'_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 + \frac{1}{2} \gamma' N \\ F'_2(N) &= v'_0 + B'_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 - \frac{1}{2} \gamma' (N+1) \end{aligned} \quad (17)$$

where

$$\begin{aligned} v'_0 &= v_0 + \frac{\sum |\xi|^2}{H}; \quad B'_\Sigma = B_\Sigma + 8 \frac{\sum |\eta|^2}{H}; \quad \gamma' = \gamma - 4 \frac{\sum \xi \eta^* + \xi^* \eta}{H} \\ \eta &= (BL_\xi)({}^2\Sigma, {}^2H); \quad \xi = (\Sigma a_l l_\xi)({}^2\Sigma, {}^2H); \quad v = v({}^2\Sigma, {}^2H) \end{aligned} \quad (17a)$$

and summation is to be extended over all vibrational levels of all perturbing 2H terms. It is apparent that, although this perturbation changes the values of the original coefficients, the dependence on the rotational quantum number remains unchanged and the doublet splitting is unaffected in consequence. It is worth while to point out that—as was shown by van Vleck—the second term in γ' (see (17a)) is usually significantly greater than the first one, and therefore the observed splitting is largely due to perturbation by the 2H terms, rather than to spin-rotation interaction.

Doublet splitting is affected, however, if one of the 2H terms comes so close to the ${}^2\Sigma$ term that the influence of the other terms can be neglected; whereas the change in $v({}^2\Sigma, {}^2H)$ vs. the rotational quantum number can no longer be neglected. According to Kovács [109, 111], Formula (17) then modifies by (2.1.2-3) and (2.1.2-4) as follows:

$$\begin{aligned} F'_1(N) &= \overline{F_1(N)} - \sigma N^2(N+1) \\ F'_2(N) &= \overline{F_2(N)} + \sigma N(N+1)^2 \end{aligned} \quad (18)$$

where $\overline{F_1(N)}$ and $\overline{F_2(N)}$ have the same form as (17), except for the coefficients:

$$\begin{aligned} \overline{F_1(N)} &= \bar{v}_0 + \bar{B}_\Sigma N(N+1) - \bar{D}_\Sigma N^2(N+1)^2 + \frac{1}{2} \bar{\gamma} N \\ \overline{F_2(N)} &= \bar{v}_0 + \bar{B}_\Sigma N(N+1) - \bar{D}_\Sigma N^2(N+1)^2 - \frac{1}{2} \bar{\gamma} (N+1) \end{aligned} \quad (19)$$

where

$$\begin{aligned} \bar{B}_\Sigma &= B_\Sigma + 8 \frac{|\eta|^2}{v} + \frac{(B_H - B_\Sigma) |\xi|^2}{v^2}; \quad \bar{D}_\Sigma = D_\Sigma - 8 \frac{(B_H - B_\Sigma) |\eta|^2}{v^2} \\ \bar{\gamma} &= \gamma - 4 \frac{\xi \eta^* + \xi^* \eta}{v}; \quad \bar{v}_0 = v_0 + \frac{|\xi|^2}{v}; \quad \sigma = 2 \frac{(B_H - B_\Sigma) (\xi \eta^* + \xi^* \eta)}{v^2} \end{aligned} \quad (20)$$

Since in Formula (19), $\overline{F_1(N)}$ and $\overline{F_2(N)}$ have the same structure as $F_1(N)$ and $F_2(N)$ in (15), experiment will provide \bar{v}_0 , \bar{B}_Σ , \bar{D}_Σ and $\bar{\gamma}$ instead of v_0 , B_Σ , D_Σ and γ . Thus $\overline{F_1(N)}$ and $\overline{F_2(N)}$ will appear as the unperturbed term values to the experimentalist.

In this case, however, the doublet splitting becomes

$$\Delta F'_{12}(N) = \overline{\Delta F_{12}(N)} - 2\sigma N(N+1)(N + \frac{1}{2}) \quad (21)$$

where

$$\overline{\Delta F_{12}(N)} = \bar{\gamma}(N + \frac{1}{2}) \quad (22)$$

The above expression differs from (16) as follows:

$$\Delta F'_{12}(N) - \overline{\Delta F_{12}(N)} = -2\sigma N(N+1)(N + \frac{1}{2}) \quad (23)$$

By taking into account also the centrifugal effect, Mulliken and Christy [159] obtained a similar expression in their model analysis.

Deviations of the above type were found by Hulthén [82] at the levels $v'' = 0, 1, 2$ in the $X^2\Sigma^+$ ground state of the HgH molecule, and also by Uhler and Åkerlind [207] at the $v' = 0$ level of the $B^2\Sigma$ term of the YO molecule. Two of these deviations are shown in Figs 2.3 and 2.4 (Kovács [109, 111]). The fit between experiment and theory is seen to be fairly good.

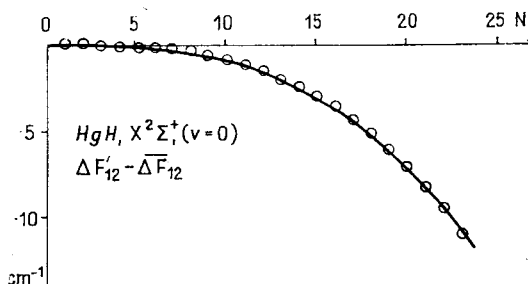


Fig. 2.3 Deviation from the usual doublet splitting observed at the $v = 0$ level of $X^2\Sigma^+$ in the HgH molecule, according to Kovács [109, 111].

In Eq. (23) of the theoretical curve,
 $\sigma = 4.24 \times 10^{-4} \text{ cm}^{-1}$.

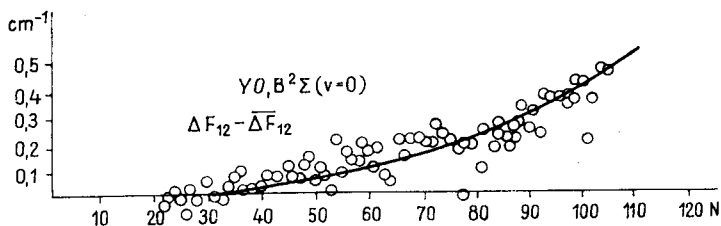


Fig. 2.4 Deviation from the usual doublet splitting observed at the $v=0$ level of $B^2\Sigma$, in the YO molecule, according to Kovács [109, 111]. In Eq. (23) of the theoretical curve, $\sigma = -1.92 \times 10^{-7} \text{ cm}^{-1}$.

2H Terms. In most cases quantities D and γ are so small that the deviations caused by them are observable only at higher rotational quantum numbers. In such cases, however, the terms 2H (and $^2\Lambda$) generally fall close to case b , so that the case b approximation of the correction terms as given by (7) and (11) proves adequate.

For the 2H terms James [90] derived more accurate formulas by taking into account the interaction between rotation and vibration.

(b) Λ -Type Doubling. When $\Lambda > 0$, both $F_1(J)$ and $F_2(J)$ are twofold degenerate. In the case of 2H terms, perturbation by the $^2\Sigma$ terms affects the coinciding components differently and therefore a splitting (Λ -type doubling) occurs. Accounting for the terms neglected on the separation of the wave equation and also for the spin-orbit interaction, perturbation

calculation leads by (1.5-10) to two secular equations which by (2.1.1-1c and d) take the following form according to van Vleck [211] and Kovács [102]:

$$\begin{array}{c} {}^2\Pi_{3/2} \\ {}^2\Pi_{1/2} \\ {}^2\Sigma_{J\pm 1/2} \end{array} \left| \begin{array}{ccc} T_1^0 - T & H_{12}^0 & \vdots & H_{13} \\ H_{21}^0 & T_2^0 - T & \vdots & H_{23}^\pm \\ \dots & \dots & \dots & \dots \\ H_{31} & H_{32}^\pm & T_3^\pm - T & \end{array} \right| = 0 \quad (24)$$

where

$$\begin{aligned} T_3^\pm &= \nu + B_\Sigma(J \pm 1/2)(J + 3/2); & T_3^- &= \nu + B_\Sigma(J - 1/2)(J + 1/2) \\ H_{23}^\pm &= \xi + 2\eta(J \pm 3/2); & H_{23}^- &= \xi - 2\eta(J - 1/2) \\ H_{13} &= -2\eta \sqrt{(J - 1/2)(J + 3/2)} \end{aligned} \quad (25)$$

The other elements are the same as in (1). The transformation by (1.5-23) into the diagonal form of the sub-matrix in the box in (24) yields

$$\begin{array}{c} {}^2\Pi_{J-1/2} \\ {}^2\Pi_{J+1/2} \\ {}^2\Sigma_{J\pm 1/2} \end{array} \left| \begin{array}{ccc} T_1 - T & 0 & H_{13}^{\pm'} \\ 0 & T_2 - T & H_{23}^{\pm'} \\ H_{31}^{\pm'} & H_{32}^{\pm'} & T_3^\pm - T \end{array} \right| = 0 \quad (26)$$

where, by (1.5-21),

$$\begin{aligned} T_3^{\pm'} &= T_3^\pm; & H_{13}^{\pm'} &= S_{3/2, J-1/2} H_{13} + S_{1/2, J-1/2} H_{23}^\pm \\ H_{23}^{\pm'} &= S_{3/2, J+1/2} H_{13} + S_{1/2, J+1/2} H_{23}^\pm \end{aligned} \quad (27)$$

and the explicit forms of T_1 and T_2 are taken from (4) (where ν_0 can be neglected). Disregarding the value of the spin doublet, (26) yields the following first approximation for the A -splitting:

$$\begin{aligned} \Delta\nu({}^2\Pi_{J-1/2}) &= \frac{|H_{13}^{\pm'}|^2 - |H_{13}^{-'}|^2}{\nu({}^2\Pi; {}^2\Sigma)} \\ \Delta\nu({}^2\Pi_{J+1/2}) &= \frac{|H_{23}^{\pm'}|^2 - |H_{23}^{-'}|^2}{\nu({}^2\Pi; {}^2\Sigma)} \end{aligned} \quad (28)$$

Written out in detail, this assumes the form

$$\Delta\nu({}^2\Pi_N) = 2(J + 1/2) [S_{1/2, N}^2(C_1 + C_2) + S_{1/2, N} S_{3/2, N} C_2 \sqrt{(J - 1/2)(J + 3/2)}] \quad (29)$$

where $N = J - 1/2, J + 1/2$; furthermore

$$\begin{aligned} C_1 &= 2 \sum_k \frac{(-1)^x [\xi \eta^* + \xi^* \eta]}{\nu}; & C_2 &= 8 \sum_k \frac{(-1)^x |\eta|^2}{\nu} \\ \xi &= (\Sigma a_i l_{i\xi})({}^2\Pi; {}^2\Sigma_k); & \eta &= (BL_\xi)({}^2\Pi; {}^2\Sigma_k); & \nu &= \nu({}^2\Pi; {}^2\Sigma_k) \end{aligned} \quad (30)$$

where $\Sigma = 0$ or 1, according as the ${}^2\Sigma$ term is ${}^2\Sigma^+$ or ${}^2\Sigma^-$. Mulliken and Christy [159] conformed Formula (29) by numerous experimental observations. One of these, the Λ -type doublet of one of the ${}^2\Pi$ terms of the ZnH molecule, is shown in Fig. 2.5.

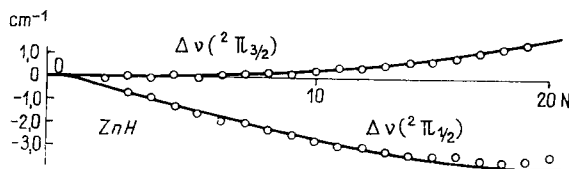


Fig. 2.5 Λ -type doubling of one of the ${}^2\Pi$ terms of the ZnH molecule, according to Mulliken and Christy [159]. In Eq. (29) of the theoretical curve, $C_1 = 0.138 \text{ cm}^{-1}$, $C_2 = 0.004 \text{ cm}^{-1}$.

Expression (29) becomes very simple in *Hund's* limiting cases. Thus in case *a*, substitution of $Y \rightarrow \infty$ into the S 's yields

$$\begin{aligned}\Delta v({}^2\Pi_{3/2}) &= 0 \\ \Delta v({}^2\Pi_{1/2}) &= 2(C_1 + C_2)(J + 1/2)\end{aligned}\quad (31)$$

In a higher-order approximation, ${}^2\Pi_{3/2}$ exhibits a very slight splitting proportional to the third power of the rotational quantum number (Mulliken and Christy [159]); a power-series expansion of (29) for $Y \gg 1$ yields for this splitting

$$\Delta v({}^2\Pi_{3/2}) = 2 \left(\frac{C_1}{Y^2} + \frac{C_2}{Y} \right) (J - 1/2)(J + 1/2)(J + 3/2) \quad (32)$$

In case *b*, substituting $Y = 0$ in the S elements of Formula (29) we obtain (cf. Kovács [102])

$$\begin{aligned}\Delta v({}^2\Pi_{J-1/2}) &= C_2 N(N+1) - C_1 N \\ \Delta v({}^2\Pi_{J+1/2}) &= C_2 N(N+1) + C_1(N+1)\end{aligned}\quad (33)$$

Since in the pure case *b*, Formula (14) will, apart from a constant, be of the same form in v_0 , B and in good approximation in γ as (15), (33) can also be interpreted by saying that the Λ -type doublet appears as if B and γ were slightly modified in the originally coinciding components. This is a result similar to that obtained for singlet terms (cf. 2.1.2-10).

Mulliken and Christy [159] studied the change in C_1 and C_2 vs. the rotational quantum number for increased rotation, i.e. as a result of the centrifugal effect upon the model. Quantum-mechanically this can be treated in the same way as the deviation from doublet splitting in the case of the ${}^2\Sigma$ terms; cf. from (17) to (23).

2.1.4. Triplet Terms

(a) **General Theory of Spin Splitting.** The term values intermediate between *Hund's* cases *a* and *b*, using (1.5-10), are obtained by solving the secular determinant

$$\Omega \begin{vmatrix} A-1 & T_1^0 - T & H_{12}^0 & 0 \\ A & H_{21}^0 & T_2^0 - T & H_{23}^0 \\ A+1 & 0 & H_{32}^0 & T_3^0 - T \end{vmatrix} = 0 \quad (1)$$

The explicit forms of the case *a* term values T_1^0, T_2^0, T_3^0 , along the diagonal and of the non-diagonal elements are, by (2.1.1-1a, b)

$$\begin{aligned} T_1^0 &= v_0 - AA + B[J(J+1) - A(A-2)] \\ T_2^0 &= v_0 + B[J(J+1) - (A-1)(A+1) + 1] \\ T_3^0 &= v_0 + AA + B[J(J+1) - A(A+2)] \\ H_{12}^0 &= B\sqrt{2[J(J+1) - (A-1)A]}; \quad H_{23}^0 = B\sqrt{2[J(J+1) - A(A+1)]} \end{aligned} \quad (2)$$

According to Kovács and Singer [128], the solution of (1) is in a fairly good approximation

$$\begin{aligned} T_1 &= \frac{T_1^0 + T_2^0 + T_3^0}{3} - \sqrt{a} - \frac{b}{2a} + \sum_{n=2}^{\infty} (-1)^n C_n \\ T_2 &= \frac{T_1^0 + T_2^0 + T_3^0}{3} + \frac{b}{a} + \sum_{n=2}^{\infty} [1 - (-1)^n] C_n \\ T_3 &= \frac{T_1^0 + T_2^0 + T_3^0}{3} + \sqrt{a} - \frac{b}{2a} - \sum_{n=2}^{\infty} C_n \end{aligned} \quad (3)$$

where

$$C_n = \frac{3}{2n} \binom{3/2n - 5/2}{n-1} \frac{b^n}{a^{1/2(3n-1)}} \quad (4)$$

and

$$\begin{aligned} a &= \frac{1}{6}(T_{12}^2 + T_{23}^2 + T_{31}^2) + |H_{12}^0|^2 + |H_{23}^0|^2 \\ b &= \frac{1}{3} \left\{ \left[\left(\frac{T_{12}}{3} \right)^2 + |H_{12}^0|^2 \right] (T_{31} + T_{32}) + \left[\left(\frac{T_{23}}{3} \right)^2 + |H_{23}^0|^2 \right] (T_{12} + T_{13}) + \right. \\ &\quad \left. + \left[\left(\frac{T_{31}}{3} \right)^2 + |H_{31}^0|^2 \right] (T_{23} + T_{21}) \right\} \\ T_{ik} &= T_i^0 - T_k^0 \end{aligned} \quad (5)$$

Substituting by their explicit forms the symbols in (3) yields the triplet formula of Budó [18]:

$$\begin{aligned}
 T_{J-1}(J) &= v_0 + B \left[-A^2 + \frac{2}{3} + J(J+1) - \sqrt{y_1 + 4J(J+1)} \right. \\
 &\quad \left. - \frac{2}{3} \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} + \dots \right] \\
 T_J(J) &= v_0 + B \left[-A^2 + \frac{2}{3} + J(J+1) + \frac{4}{3} \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} + \dots \right] \quad (6) \\
 T_{J+1}(J) &= v_0 + B \left[-A^2 + \frac{2}{3} + J(J+1) + \sqrt{y_1 + 4J(J+1)} \right. \\
 &\quad \left. - \frac{2}{3} \frac{y_2 - 2J(J+1)}{y_1 + 4J(J+1)} + \dots \right]
 \end{aligned}$$

where

$$y_1 = A^2 Y(Y-4) + \frac{4}{3}; \quad y_2 = A^2 Y(Y-1) - \frac{4}{9} \quad (7)$$

and $Y = A/B$. With $A > 0$, the term is normal; with $A < 0$, it is inverted.

By (6) and (1.5-9), the elements of the transformation matrix can be formed as

$$\begin{aligned}
 S_{A-1, J-1} &= \sqrt{\frac{(J-A+1)(J+A)}{4C_1(J)}} u_1^+(J) \\
 S_{A, J-1} &= - \sqrt{\frac{2(J-A)^2(J+A)^2}{C_1(J)}} \\
 S_{A+1, J-1} &= \sqrt{\frac{(J-A)(J+A+1)}{4C_1(J)}} u_1^-(J) \\
 S_{A-1, J} &= \sqrt{\frac{2(J-A+1)(J+A)}{C_2(J)}} \\
 S_{A, J} &= \sqrt{\frac{A^2(Y-2)^2}{C_2(J)}} \quad (8) \\
 S_{A+1, J} &= - \sqrt{\frac{2(J-A)(J+A+1)}{C_2(J)}} \\
 S_{A-1, J+1} &= \sqrt{\frac{(J-A+1)(J+A)}{4C_3(J)}} u_3^-(J) \\
 S_{A, J+1} &= \sqrt{\frac{2(J-A+1)^2(J+A+1)^2}{C_3(J)}} \\
 S_{A+1, J+1} &= \sqrt{\frac{(J-A)(J+A+1)}{4C_3(J)}} u_3^+(J)
 \end{aligned}$$

where

$$u_1^\mp(J) = [A^2 Y(Y-4) + 4J^2]^{1/2} \pm A(Y-2)$$

$$u_3^\pm(J) = [A^2 Y(Y-4) + 4(J+1)^2]^{1/2} \pm A(Y-2) \quad (9)$$

and

$$C_1(J) = A^2 Y(Y-4) (J-A+1) (J+A) + 2(2J+1) (J-A) J(J+A)$$

$$C_2(J) = A^2 Y(Y-4) + 4J(J+1)$$

$$C_3(J) = A^2 Y(Y-4) (J-A) (J+A+1) + 2(2J+1) (J-A+1) \times \\ \times (J+1) (J+A+1) \quad (10)$$

In the case of inverted terms, Y is to be replaced by $-Y$ and A by $-A$ in expression (10). The simpler forms of the transformation matrix for cases a and b can be obtained by the substitutions $Y \rightarrow \pm \infty$ (normal and inverted) and $Y = 0$, respectively.

The formulas in (6) are to be complemented by some correction terms in more rigorous investigations. The first correction is the centrifugal term already discussed for the doublet terms. The form of the centrifugal term for *Hund's* case b is the same as in (2.1.1-6) except that now the substitutions are $N = J-1, J, J+1$. Since, however, for $A > 0$ the terms are usually intermediate between *Hund's* cases a and b , it is necessary to derive also the intermediate form of the centrifugal correction. To do so, we start again from the case a forms of (2.1.1-2a, b, c), first derived for the $^3\Pi$ term by Gilbert [66]; his derivation was applied by Almy and Horsfall [9] to the doublet case. We shall adopt a different procedure also in the present case of triplets. A general form valid for any type of triplet term is as follows:

$$H_{A+1, A+1}^c = -D\{[J(J+1) - A(A+2)]^2 + 2[J(J+1) - A(A+1)]\}$$

$$H_{A, A}^c = -D\{[J(J+1) - (A-2)(A+2)]^2 - 12\}$$

$$H_{A-1, A-1}^c = -D\{[J(J+1) - A(A-2)]^2 + 2[J(J+1) - A(A-1)]\}$$

$$H_{A+1, A}^c = H_{A, A+1}^c = -2D\{J(J+1) + 1 - A(A+1)\} \times$$

$$\times \sqrt{2(J-A)(J+A+1)} \times$$

$$H_{A, A-1}^c = H_{A-1, A}^c = -2D\{J(J+1) + 1 - A(A-1)\}$$

$$\times \sqrt{2(J-A+1)(J+A)}$$

$$H_{A+1, A-1}^c = H_{A-1, A+1}^c = -2D\sqrt{(J-A)(J-A+1)(J+A)(J+A+1)}$$

(11)

Gilbert added (11) to (1) and studied the secular equation so obtained. This was so complicated, however, that he was unable to give the explicit expressions of the term values; he could give only a method for the determination of the rotational constants B and D , and of the coupling constant A . We can, however, with the method resorted to in connexion with (1.5-15), and using formulas (8) and (11), give the explicit form of the centrifugal term for the intermediate case between *Hund's* cases a and b , without upsetting the structure of (6):

$$H_N^c(J) = S_{A+1,N}^2 H_{A+1,A+1}^c + S_{A,N}^2 H_{A,A}^c + S_{A-1,N}^2 H_{A-1,A-1}^c \\ + 2S_{A+1,N} S_{A,N} H_{A+1,A}^c + 2S_{A,N} S_{A-1,N} H_{A,A-1}^c + 2S_{A+1,N} S_{A-1,N} H_{A+1,A-1}^c \quad (12)$$

where $N = J - 1, J, J + 1$. Formula (12) can simply be added to (6). For $Y = 0$, Formula (12) reduces to (2.1.1-6), whereas for $Y \rightarrow \infty$ it yields the diagonal elements of (11).

Since terms of higher multiplicity than the doublet have more than one electron outside the closed shell, the interaction between the spins of the electrons has to be taken into account too. Some of the appropriate forms were given for *Hund's* case a by Kramers [132], and some by Hebb [68]. For a triplet, this assumes by (2.1.1-3a) and (2.1.1-3b) the form

$$H_a^{ss} = \varepsilon[3\Sigma^2 - 2] \pm \delta_{0,\Omega} \delta_{1,\Lambda} \alpha \quad (13)$$

where $\Sigma = -1, 0, +1$. The first term of (13) corresponds to the transition $\Lambda\Lambda = \Lambda\Sigma = 0$, and the second term to $\Lambda\Lambda = -\Lambda\Sigma = \pm 2$. The latter occurs only in the case of Π terms, between ${}^3\Pi_0$ ($\Lambda = +1, \Sigma = -1$) and ${}^3\Pi'_0$ ($\Lambda = -1, \Sigma = +1$).

The case b form can be derived from (2.1.1-7a, b) by putting $S = 1$. The intermediate form of this interaction, as first derived from (1.5-15) by Kovács [101], and subsequently complemented, is

$$H_N^{ss}(J) = \varepsilon - 3\varepsilon S_{A,N}^2 \pm \delta_{1,\Lambda} \alpha S_{A-1,N}^2 \quad (14)$$

where $N = J - 1, J, J + 1$ and $S_{A,N}$ and $S_{A-1,N}$ are to be taken from (8). It is practical to incorporate the first term on the right-hand side into the value of ν_0 , as it would be rather difficult to determine it separately; cf. (27).

A further correction arises from the interaction between rotation and spin. The case b form can again be derived from (2.1.1-8); the case a form necessary to write up the intermediate form is, by (2.1.1-4a, b),

$$H_a^{sr} = \begin{vmatrix} -\gamma & -\frac{\gamma}{\sqrt{2}} \sqrt{(J+A)(J-A+1)} & 0 \\ -\frac{\gamma}{\sqrt{2}} \sqrt{(J+A)(J-A+1)} & -2\gamma & -\frac{\gamma}{\sqrt{2}} \sqrt{(J-A)(J+A+1)} \\ 0 & -\frac{\gamma}{\sqrt{2}} \sqrt{(J-A)(J+A+1)} & -\gamma \end{vmatrix} \begin{matrix} \Omega \\ A-1 \\ A \\ A+1 \end{matrix} \quad (15)$$

By (8) and (1.5-15) we obtain from (15) for the intermediate case

$$H_N^{ss}(J) = -\gamma [1 + S_{A,N}^2 + S_{A+1,N} S_{A,N} \sqrt{2(J-A)(J+A+1)} + \\ + S_{A,N} S_{A-1,N} \sqrt{2(J+A)(J-A+1)}] \quad (16)$$

where again $N = J - 1, J, J + 1$. In *Hund's case b* ($Y = 0$) formula (16) reduces to (2.1.1-8); in case *a* ($Y \rightarrow \infty$) it yields the diagonal elements of (15). Expression (16) is also to be added to (6).

Accordingly, the full term formula for the triplet case is

$$F_N(J) = T_N(J) + H_N^e(J) + H_N^{ss}(J) + H_N^{ss}(J) \quad (17)$$

where $N = J - 1, J, J + 1$.

$^3\Sigma$ Terms. Putting $A = 0$ and $Y = 0$ in Formula (17), the term formulas valid for the $^3\Sigma$ terms are obtained:

$$F_{J-1}(N) = F_1(N) = v_0 + B_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 - \varepsilon \frac{N}{2N+3} + \gamma N \\ F_J(N) = F_2(N) = v_0 + B_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 + \varepsilon - \gamma \\ F_{J+1}(N) = F_3(N) = v_0 + B_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 - \\ - \varepsilon \frac{N+1}{2N-1} - \gamma(N+1) \quad (18)$$

These are in effect the formulas given by Kramers [131]. We can obtain simple, analytically closed formulas for the $^3\Sigma$ terms by adding (13) to (1); the secular equation so obtained can be solved rigorously, as it decomposes into a second-order and a first-order equation, the solutions of which are, according to Schlapp [194],

$$T_{J-1}(N) = v_0 + B_\Sigma \left[N(N+1) + (2N+3) - \right. \\ \left. - \sqrt{\frac{3\varepsilon}{B_\Sigma} \left(\frac{3\varepsilon}{4B_\Sigma} - 1 \right) + (2N+3)^2} \right] - \frac{\varepsilon}{2} \\ T_J(N) = v_0 + B_\Sigma N(N+1) + \varepsilon \quad (19) \\ T_{J+1}(N) = v_0 + B_\Sigma \left[N(N+1) - (2N-1) + \right. \\ \left. + \sqrt{\frac{3\varepsilon}{B_\Sigma} \left(\frac{3\varepsilon}{4B_\Sigma} - 1 \right) + (2N-1)^2} \right] - \frac{\varepsilon}{2}$$

These formulas are more accurate than (18) especially if the coefficient of the spin-spin interaction, ε , compared with B_Σ is not too small. If, moreover, ε is greater than B_Σ , and hence, in comparison also with D_Σ and γ , the coefficients of the other two interactions are great, then the case b form no longer gives sufficiently accurate formulas. Here again, using (from 1.5-11 to 1.5-15) the spin-spin interaction is to be attributed the role of perturbation operator of higher order magnitude, rather than the spin-orbit interaction. Using the newly derived transformation-matrix elements, the expressions for the centrifugal term and for the interaction between the rotation and the spin are now to be calculated by (1.5-15). In this case, the expressions (17) of $F_{J-1}(N)$ and $F_{J+1}(N)$ will be modified by the introduction, beside the expressions (19), of the following more accurate expressions in the place of $-D_\Sigma N^2(N+1)^2$ and γN :

$$H_{J\mp 1}^c(J) = -\frac{D_\Sigma}{u^\pm(J)^2 + 4J(J+1)} \{4J^2(J+1)^2[J(J+1) + 4] - 16J(J+1)[J(J+1) + 1]u^\pm(J) + [(J(J+1) + 4)^2 - 12]u^\pm(J)^2\} \quad (19a)$$

$$H_{J\mp 1}^s(J) = -\gamma \left\{ 1 + u^\pm(J) \frac{u^\pm(J) - 4J(J+1)}{u^\pm(J)^2 + 4J(J+1)} \right\} \quad (19b)$$

$$u^\pm(J) = \frac{3\varepsilon}{2B_\Sigma} - 1 \pm \sqrt{\frac{3\varepsilon}{B_\Sigma} \left(\frac{3\varepsilon}{4B_\Sigma} - 1 \right) + (2J+1)^2} \quad (19c)$$

The above formulas can be rewritten in terms of N by substituting $J = N \pm 1$ on the right-hand sides. Expressions (19a) and (19b) yield the case b forms of the above interactions for $\varepsilon=0$ and the case a forms for $\varepsilon \rightarrow \infty$.

As an experimental application, the spin splitting at the $v=0$ level of the $^3\Sigma^-$ term in the transition $^3\Pi-^3\Sigma^-$, observed by Funke [55] at 3360 Å in the spectrum of the NH molecule, is shown in Fig. 2.6. The solid curves are calculated by Formulas (19).

In some cases, however, experiment has revealed deviations from the above formulas (19a) and (19b), the reason to be given below.

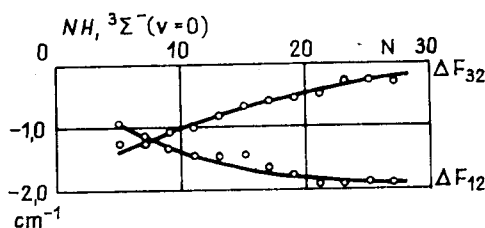


Fig. 2.6 Spin splitting observed at the $v=0$ level of $^3\Sigma^-$ in the NH molecule, according to Funke [55]. The upper curve represents F_3-F_2 ; the lower one represents F_1-F_2 . In Eq. (19) of the theoretical curve, $B_\Sigma=16.33$ cm^{-1} , $D_\Sigma = -1.67 \times 10^{-3}$ cm^{-1} , $\varepsilon = 0.45$ cm^{-1} and $\gamma = -0.04$ cm^{-1} .

Examining the effects of perturbation by farther-lying terms, it is found that these will affect the constants in (18). Thus in the case of perturbation by the $^3\Pi$

terms the term formulas become (Hebb [68], Kovács [109])

$$\begin{aligned} F'_1(N) &= v'_0 + B'_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 - \varepsilon' \frac{N}{2N+3} + \gamma' N \\ F'_2(N) &= v'_0 + B'_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 + \varepsilon' - \gamma' \\ F'_3(N) &= v'_0 + B'_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 - \varepsilon' \frac{N+1}{2N-1} - \gamma'(N+1) \end{aligned} \quad (20)$$

where

$$\begin{aligned} v'_0 &= v_0 + \frac{2}{3} \frac{\sum}{H} \frac{|\xi|^2}{v}; \quad B'_\Sigma = B_\Sigma + 8 \frac{\sum}{H} \frac{|\eta|^2}{v}; \quad \varepsilon' = \varepsilon - \frac{\sum}{H} \frac{|\xi|^2}{6v} \\ \gamma' &= \gamma - 2 \frac{\sum}{H} \frac{\xi\eta^* + \xi^*\eta}{v}; \quad \xi = (\Sigma a_{l_i \xi}) ({}^3\Sigma; {}^3I_k) \\ \eta &= (BL_\xi) ({}^3\Sigma; {}^3I_k); \quad v = v ({}^3\Sigma, {}^3I_k) \end{aligned} \quad (21)$$

The dependence on the rotational quantum number is the same as in (18). If, however, one of the above 3H terms is sufficiently close to the ${}^3\Sigma$ term, allowing the effects of all other terms to be neglected, then v will be affected by the change in the rotational quantum number and by (2.1.3-3) and (2.1.3-4), Formula (20) modifies as follows (Kovács [109, 111]):

$$\begin{aligned} F'_1(N) &= \overline{F}_1(N) - [\sigma(N+1) - \tau] N(N+1) \\ F'_2(N) &= \overline{F}_2(N) \\ F'_3(N) &= \overline{F}_3(N) + [\sigma N + \tau] N(N+1) \end{aligned} \quad (22)$$

where $\overline{F}_1(N)$, $\overline{F}_2(N)$ and $\overline{F}_3(N)$ are formally the same as (20), but the constants are different:

$$\begin{aligned} \overline{v}_0 &= v_0 + \frac{2}{3} \frac{|\xi|^2}{v}; \quad \overline{B}_\Sigma = B_\Sigma + \frac{8|\eta|^2}{v} - 2 \frac{\xi\eta^* + \xi^*\eta}{v^2} (B_\Sigma - B_\Pi) - \frac{|\xi|^2}{2v^2} (B_\Sigma - B_\Pi) \\ \overline{D}_\Sigma &= D_\Sigma - 8 \frac{|\eta|^2}{v^2} (B_\Sigma - B_\Pi); \quad \overline{\varepsilon} = \varepsilon - \frac{|\xi|^2}{6v}; \quad \overline{\gamma} = \gamma - 2 \frac{\xi\eta^* + \xi^*\eta}{v} \end{aligned} \quad (23)$$

and

$$\sigma = 2 \frac{\xi\eta^* + \xi^*\eta}{v^2} (B_\Pi - B_\Sigma); \quad \tau = \frac{|\xi|^2}{4v^2} (B_\Pi - B_\Sigma) \quad (24)$$

where now $v = v ({}^3\Sigma, {}^3H)$ means the unchanged vibrational distance between the unique 3H term and the ${}^3\Sigma$ term. Since the structure of $\overline{F}_1(N)$, $\overline{F}_2(N)$, $\overline{F}_3(N)$ is the same as that of (18), the experimental data will provide v_0 , \overline{B}_Σ , \overline{D}_Σ , $\overline{\varepsilon}$, $\overline{\gamma}$ instead of v_0 , B_Σ , D_Σ , ε , γ ; in other words, $\overline{F}_1(N)$, $\overline{F}_2(N)$, $\overline{F}_3(N)$ can be regarded as unperturbed values.

In this case, however, the triplet splitting differs from the unperturbed triplet splitting as follows:

$$\begin{aligned} \Delta F'_{12} - \overline{\Delta F}_{12} &= -[\sigma(N+1) - \tau] N(N+1) \\ \Delta F'_{32} - \overline{\Delta F}_{32} &= [\sigma N + \tau] N(N+1) \end{aligned} \quad (25)$$

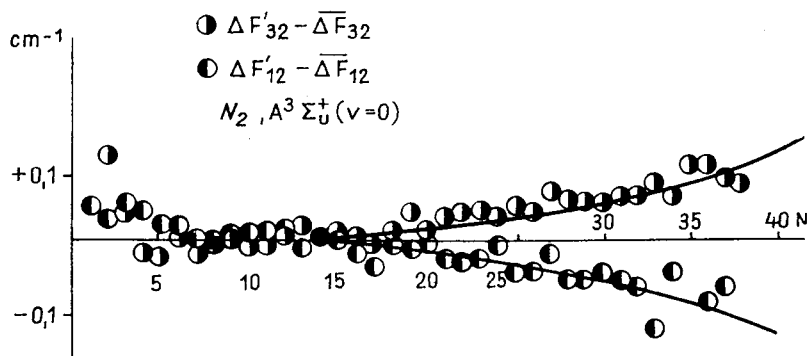


Fig. 2.7 Deviation from the usual spin splitting at the $v=0$ level of $A^3\Sigma_u^+$ in the N_2 molecule, according to Kovács [109, 111]. In Eq. (25) of the theoretical curve, $\sigma = 1.9 \times 10^{-6} \text{ cm}^{-1}$, $\tau = -1.8 \times 10^{-6} \text{ cm}^{-1}$.

Such deviations were observed by Carroll [29] at the vibrational levels $v = 0, 1, 2$ of the term $A^3\Sigma_u^+$ of the N_2 molecule. The deviations found at the $v = 0$ level and the theoretical curves calculated by Kovács [109, 111] using formula (25) are shown in Fig. 2.7.

The consideration of the spin-orbit interaction, among the other terms, renders possible perturbations by the terms $^1\Sigma$, $^1\Pi$, $^3\Sigma$, $^5\Sigma$ and $^5\Pi$. These, however, affect only v_0 and ϵ . If one of these terms comes close to the original $^3\Sigma$ term, then by (2.1.2-3) and (2.1.2-4), the triplet splitting is again modified, but to a smaller extent than in the previous case. The splitting is described by (25) except that now $\sigma = 0$ is to be substituted, yielding

$$\Delta F'_{12} - \overline{\Delta F}_{12} = \Delta F'_{32} - \overline{\Delta F}_{32} \approx \tau N(N+1) \quad (26)$$

where τ has a meaning similar to that in (23), except that now $v(^3\Sigma; X)$ and B_X are to be written instead of v and B_{II} , respectively; X is the term that causes the perturbation. An example for this effect is found again in the N_2 molecule, at the $v = 5$ vibrational level of the $B'^3\Sigma_u$ term (Carroll and Rubalcava [32]). Figure 2.8 shows this effect together with the theoretical curve calculated by Kovács [109, 111]. Tinkham and Strandberg [205] also discussed ways of obtaining more accurate $^3\Sigma$ term formulas.

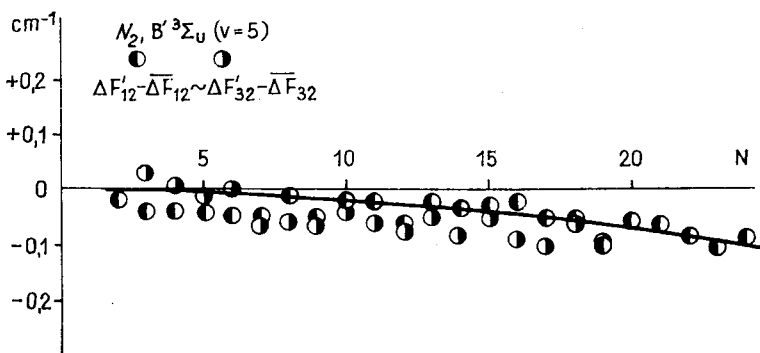


Fig. 2.8 Deviation from the usual spin splitting, observed on the $v=5$ level of $B'^3\Sigma_u$ in the N_2 molecule, according to Kovács [109, 111]. In Eq. (26) of the theoretical curve, $\tau = -1.53 \times 10^{-4} \text{ cm}^{-1}$.

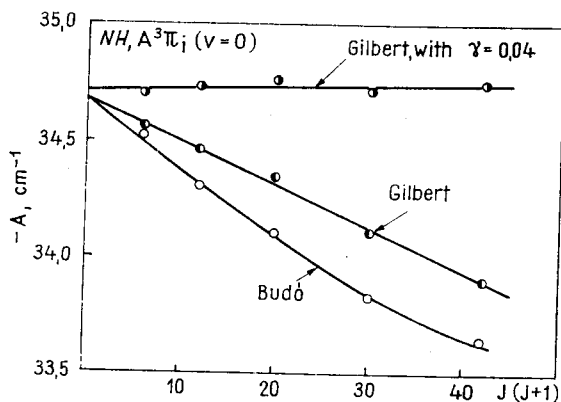


Fig. 2.9 The coupling constant A at the $v=0$ level of $A^3\Pi_i$ in the NH molecule, vs. the rotational quantum number, according to Dixon [46]. If, in addition to the Gilbert formula, expression (16) is taken into account with $\gamma = 0.04$ cm^{-1} , the change in A disappears.

$^3\Pi$ and $^3\Delta$ Terms. Putting $A = 1$ and 2 in Formula (17) we obtain the term formulas valid for the terms $^3\Pi$ and $^3\Delta$, respectively. The validity of the first term, (6), in the expression (17) has been verified in several experiments, such as those involving the triplet terms of the molecules N_2 , C_2 , CO , AlH (Budó [18, 19]). Wherever a deviation from (6) was detected, and the reason for the deviation could be established, it was found that the correction terms either were not applied at all or were applied in

a wrong way. The deviation usually consists in that the multiplet-splitting constant A or, in other words, the spin-orbit coupling constant apparently varies with the rotational quantum number.

The centrifugal term is usually taken into account in the form $DJ^2/(J+1)^2$ for Hund's case a (which approximation is sufficient only if D is very small). The centrifugal term was computed with the method of Gilbert [66], essentially equivalent to Formula (12), for such molecules as AlH , OH^+ and BH (Challacombe and Almy [33]). For the molecules NH (Dixon [46]), OH^+ (O'Connor [172]) and CO (Carroll [30]) it was necessary to apply to the terms $^3\Pi$ and $^3\Delta$ also the correction given by (16) for the spin-rotation interaction. The 'change' in constant A vs. the rotational quantum number for the $^3\Pi$ term of the NH molecule (after Dixon [46]) is shown in Fig. 2.9. The figure is highly instructive for a number of reasons.

Firstly, there is a clear-cut difference between Budó's formula and Gilbert's procedure, the reason for which is that the centrifugal correction has not been applied to Budó's formula in its form (12). Secondly, the change in A disappears when the interaction between rotation and spin is also taken into consideration. Thirdly, the value of A obtained in this way is still not satisfactory as the spin-spin interaction has not yet been taken into account.

Neglect of the spin-spin interaction has led in several other cases to substantial deviations from the formulas given by Budó and Gilbert. Such deviations were observed in the $^3\Pi$ terms of NH (Dixon [46]), PH (Ishaque and Pearse [86], Legay [147]), PF (Douglas and Frackowiak [48]) and TiO (Christy [38], Phillips [176]) and in a $^3\Delta$ term of CO , too (Carroll [30]). The application of Formula (14) will, however, eliminate the 'anomalous' triplet splittings observed in these cases and the resultant coupling constant

A no longer changes with the rotational quantum number. (For more details, see the considerations below.)

If we take the spin-orbit interaction into account, expression (14) is modified by the effects of perturbation by the ${}^1\Pi$ terms in the case of the ${}^3\Pi$ terms; and by the ${}^1\Delta$ terms in the case of the ${}^3\Delta$ terms; the modified version of (14) is as follows (Kovács [106]):

$$H_N^{ss,so}(J) = \varepsilon + \beta S_{A,N}^2 \quad (27)$$

where

$$\beta = -3\varepsilon + \sum \frac{|\varrho|^2}{v} \quad (28)$$

and ϱ is the perturbation-matrix element of the spin-orbit interaction according to Formula (1.2-9b); the interaction is taken into account between terms ${}^3\Pi$ and ${}^1\Pi$ for term ${}^3\Pi$ and between terms ${}^3\Delta$ and ${}^1\Delta$ for term ${}^3\Delta$; v is the term spacing between the corresponding triplet and singlet terms.

Let us now denote the sum of the first, second and fourth terms of (17) by $F_N^*(J)$; let further $F_N(J)$ denote $F_N^*(J) + H_N^{ss,so}(J)$. Then the total deviation due to the spin-spin and spin-orbit interactions can be expressed for the triplet splittings as

$$\Delta F_{N,N+1}(J) - \Delta F_{N,N+1}^*(J) = \beta[S_{A,N}^2 - S_{A,N+1}^2] \quad (29)$$

where $N = J - 1, J$.

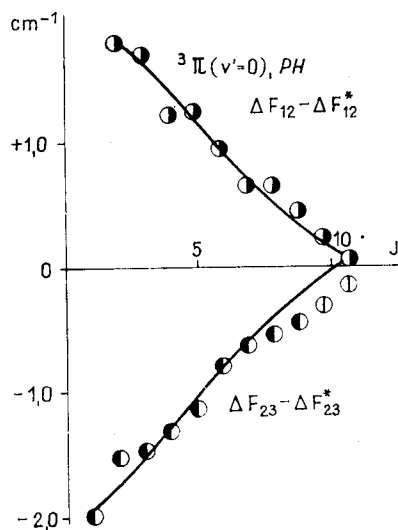


Fig. 2.10 Deviation from the usual triplet splitting observed at the $v=0$ level of one of ${}^3\Pi$ states in the PH molecule, according to Kovács [107]. In Eq. (29) of the theoretical curve, calculated with regard to the spin-orbit interaction, $\beta = -2.0 \text{ cm}^{-1}$.

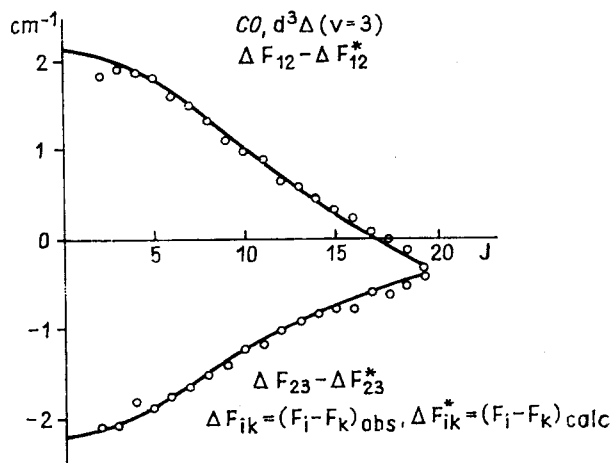


Fig. 2.11 Deviation from the usual triplet splitting observed at the $v=3$ level of $d^3\Delta$, in the CO molecule, according to Kovács [118]. In Eq. (29) of the theoretical curve calculated with regard to spin-orbit interaction, $\beta = -2.15 \text{ cm}^{-1}$.

The application of (29) to account for the deviations is described in the following papers by Kovács: NH [106], PH [107], PF [115], TiO [117] (see also paper [206] by Törös), CO [116, 118, 119]. Let us cite as examples the ${}^3\Pi$ terms of the molecule PH, and the 3A terms of CO (Figs 2.10 and 2.11).

(b) Λ -Type Doubling. In the case $\Lambda > 0$, all the term values in (17) are twofold degenerate. In the case of the ${}^3\Pi$ terms, however, the otherwise coinciding states are split up owing partly to perturbation by the ${}^3\Sigma$ terms (and also by the ${}^1\Sigma$ and ${}^5\Sigma$ terms), and partly to the spin-spin interaction affecting the state ${}^3\Pi_0$; the result is a Λ -type doublet.

In the theoretical discussion of this splitting, the taking into consideration of the terms neglected on the separation of the wave equation, and also of the spin-orbit and spin-spin interactions yields a fifth-order and a fourth-order secular equation, whose elements can be derived from (2.1.1-1a, b, c, d) and (2.1.1-3b). If, following Hebb [68], the parts of the determinants that are identical with (1) are transformed into the diagonal form by (8) and (1.5-21 and 1.5-23), then a first approximation of Λ -splitting results in the form

$$\Delta v({}^3\Pi_N) = C_0 S_{0,N}^2 + C_1 S_{1,N} S_{0,N} \sqrt{2J(J+1)} + C_2 \{ S_{1,N}^2 J(J+1) + 2S_{2,N} S_{0,N} \sqrt{(J-1)J(J+1)(J+2)} \} \quad (30)$$

where $N = J - 1, J, J + 1$; furthermore,

$$C_0 = \sum (-1)^x \frac{|\xi|^2}{\nu} - 2\alpha - \sum (-1)^{x'} \frac{|\xi'|^2}{\nu'}; C_1 = 4 \sum (-1)^x \frac{\xi \eta^* + \xi^* \eta}{\nu} \\ C_2 = 8 \sum (-1)^x \frac{|\eta|^2}{\nu} \quad (31)$$

and

$$\xi = \xi + 4\eta; \xi = (\Sigma a_i l_{i\xi})({}^3\Pi; {}^3\Sigma_k); \eta = (BL_\xi)({}^3\Pi; {}^3\Sigma_k); \nu = \nu({}^3\Pi; {}^3\Sigma_k) \\ \xi' = (\Sigma a_i l_{i\xi})({}^3\Pi; {}^x\Sigma_k); \nu' = \nu({}^3\Pi; {}^x\Sigma_k); x = 1 \text{ or } 5 \quad (32)$$

α is the matrix element of the spin-spin interaction between two ${}^3\Pi_0$ states, with the possible orientations $+\Lambda$ and $-\Lambda$; Σ and Σ' in the exponent are either 0 or 1, according as the Σ term in question is a Σ^+ or a Σ^- .

Formula (30) has been applied to many experimentally observed cases. We have illustrated here the Λ -type doubling in the $B {}^3\Pi$ state of the N_2 molecule as given by Hebb [68] (Fig. 2.12).

Formula (30) assumes a simple form in *Hund's* limiting cases. Thus for case *a* the substitution $Y \rightarrow \infty$ yields

$$\Delta v({}^3\Pi_2) = 0 \\ \Delta v({}^3\Pi_1) = C_2 J(J+1) \\ \Delta v({}^3\Pi_0) = C_0 \quad (33)$$

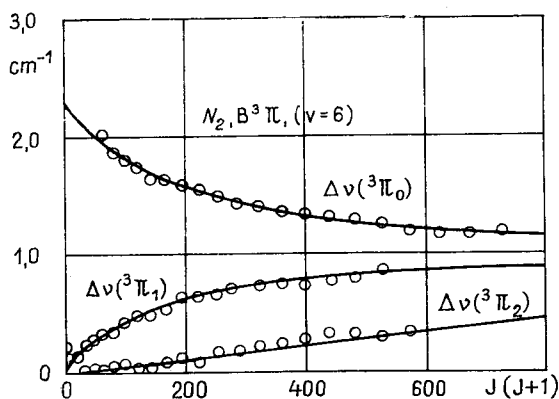


Fig. 2.12 Λ -type doubling observed on the $B^3\Pi$ state of the N_2 molecule, according to Hebb [68]. In Eq. (30) of the theoretical curve, $C_0 = 2.27 \text{ cm}^{-1}$, $C_1 = 0.0095 \text{ cm}^{-1}$, $C_2 = 0.00026 \text{ cm}^{-1}$.

For case b Kovács [101] found, by putting $Y = 0$, that

$$\begin{aligned} \Delta v(^3\Pi_{J-1}) &= \frac{1}{2}(C_0 - C_1 + 2C_2) \frac{N}{2N+3} - \frac{1}{2}(C_1 - 4C_2)N + C_2N(N+1) \\ \Delta v(^3\Pi_J) &= -\frac{1}{2}(C_0 - C_1 + 2C_2) + \frac{1}{2}(C_1 - 4C_2) + C_2N(N+1) \\ \Delta v(^3\Pi_{J+1}) &= \frac{1}{2}(C_0 - C_1 + 2C_2) \frac{N+1}{2N-1} + \frac{1}{2}(C_1 - 4C_2)(N+1) + \\ &\quad + C_2N(N+1) \end{aligned} \quad (34)$$

The part arising from the spin-spin interaction in the first term on the right-hand side of formula (34) can be directly obtained from (2.1.1-7b); see also Kovács [110]. This procedure was applied by Fontana [51] to the $C^3\Pi_u$ state of the H_2 molecule as measured by Foster and Richardson [52] and Lichten [148], and to the $^3\Pi_g$ state of the He_2 molecule as measured by Mulliken and Monk [160]. It was further applied with good results by Carroll [31] to the $C^3\Pi_u$ state of the N_2 molecule.

Since in case b the term formulas of the $^3\Pi$ state are nearly identical formally to (34), with the difference that the coefficients are ϵ , γ and B there, it can be stated that in *Hund's case b* the Λ -type splitting of the triplet terms is apparently caused—similarly as in the singlet and doublet cases—by slight changes in the constants of the separating components of the doublet.

2.1.5. *Quartet Terms*

(a) **General Theory of Spin Splitting.** The calculation of spin splitting for the intermediate case between *Hund's* cases *a* and *b* leads to a fourth-order secular equation whose diagonal contains the energies for *Hund's* case *a*; they can easily be derived, together with the non-diagonal elements, from (2.1.1-1a, b). The expansion of the determinant leads after removal of the third-order term by an appropriate transformation, to the equation

$$x^4 + bx^2 + cx + d = 0 \quad (1)$$

where

$$\begin{aligned} x &= \frac{1}{B} \{T + BA^2 - B[J(J+1) + 5/4]\} \\ b &= -10[y_1 + J(J+1) + 9/2]; \quad y_1 = 1/4 A^2 Y(Y-4) \\ c &= 8A^2 Y(Y-1) - 4 - 16J(J+1) \end{aligned} \quad (2)$$

$$d = 9[y_1 + J(J+1)]^2 - 11/2[y_1 + J(J+1)] - 3A^2 Y^2 - 12A^2 Y - 15/16$$

The solution of equation (2) was given by Brandt [16] as

$$\begin{aligned} x_1 &= - \left\{ -\frac{b}{2} + \frac{1}{2} \sqrt{b^2 - 4d} \right\}^{1/2} - \frac{c}{2} (b^2 - 4d) + \dots \\ x_2 &= - \left\{ -\frac{b}{2} - \frac{1}{2} \sqrt{b^2 - 4d} \right\}^{1/2} + \frac{c}{2} (b^2 - 4d) + \dots \\ x_3 &= \left\{ -\frac{b}{2} - \frac{1}{2} \sqrt{b^2 - 4d} \right\}^{1/2} + \frac{c}{2} (b^2 - 4d) + \dots \\ x_4 &= \left\{ -\frac{b}{2} + \frac{1}{2} \sqrt{b^2 - 4d} \right\}^{1/2} - \frac{c}{2} (b^2 - 4d) + \dots \end{aligned} \quad (3)$$

Combining (2) and (3), Brandt [16] gave for the term values the expressions

$$\begin{aligned} T_{J-3/2}(J) &= v_0 + B \left\{ J(J+1) - A^2 + 5/4 - \right. \\ &\quad \left. - \sqrt{9y_1 + 9J(J+1) + 23/4 + \delta/2} - \frac{y_2 - 2J(J+1)}{2y_1 + 7/4 + \delta/4 + 2J(J+1)} + \dots \right\} \end{aligned}$$

$$T_{J-1/2}(J) = v_0 + B \left\{ J(J+1) - A^2 + \frac{5}{4} - \right. \\ \left. - \sqrt{y_1 + J(J+1) - \frac{5}{4} - \delta/2} + \frac{y_2 - 2J(J+1)}{2y_1 + \frac{7}{4} + \delta/4 + 2J(J+1)} + \dots \right\} \quad (4)$$

$$T_{J+1/2}(J) = v_0 + B \left\{ J(J+1) - A^2 + \frac{5}{4} + \right. \\ \left. + \sqrt{y_1 + J(J+1) - \frac{5}{4} - \delta/2} + \frac{y_2 - 2J(J+1)}{2y_1 + \frac{7}{4} + \delta/4 + 2J(J+1)} + \dots \right\}$$

$$T_{J+3/2}(J) = v_0 + B \left\{ J(J+1) - A^2 + \frac{5}{4} + \right. \\ \left. + \sqrt{9y_1 + 9J(J+1) + \frac{23}{4} + \delta/2} - \frac{y_2 - 2J(J+1)}{2y_1 + \frac{7}{4} + \delta/4 + 2J(J+1)} + \dots \right\}$$

where

$$\delta = \frac{6A^2Y^2 + 24A^2Y - \frac{25}{2}}{8[y_1 + J(J+1)] + 7}; \quad y_2 = A^2Y(Y-1) - \frac{1}{2}; \quad Y = \frac{A}{B} \quad (5)$$

If $A > 0$, the term is normal; if $A < 0$, it is inverted.

Starting from case *b*, Rao [186] derived term formulas different from (4). Examining the usefulness of his formulas in the case of the $^4\Pi$ term of the O_2^+ molecule, he found that they provided a satisfactory approximation only for high rotational quantum numbers, i.e. in the vicinity of case *b*. His formulas are not given here since (4) provides a better approximation.

The elements of the transformation matrix can be derived from (4) and (1.5-9) as was first done by Budó and Kovács [25]. Generalized to cover quartet terms of any type, the matrix elements are of the form

$$S_{i,N} = s_{i,N} (s_{A-3/2,N}^2 + s_{A+1/2,N}^2 + s_{A-1/2,N}^2 + s_{A-3/2,N}^2)^{-1/2} \quad (6)$$

where $i = A - 3/2, A - 1/2, A + 1/2, A + 3/2$ and

$$s_{A-3/2,N} = 2[3(J + A + 1/2)(J - A + 1/2)(J + A - 1/2)(J - A + 3/2)]^{1/2} \times \\ \times (T_{A+3/2}^a - T_N)$$

$$s_{A-1/2,N} = -2[(J + A + 1/2)(J - A + 1/2)]^{1/2} (T_{A-3/2}^a - T_N)(T_{A-3/2}^a - T_N)$$

$$s_{A+1/2,N} = (T_{A+3/2}^a - T_N)[(T_{A-1/2}^a - T_N)(T_{A-3/2}^a - T_N) - 3(J + A - 1/2) \times \\ \times (J - A + 3/2)]$$

$$s_{A+\frac{3}{2},N} = -[3(J-A-\frac{1}{2})(J+A+\frac{3}{2})]^{1/2}[(T_{A-\frac{1}{2}}^a - T_N)(T_{A-\frac{3}{2}}^a - T_N) - 3(J+A-\frac{1}{2})(J-A+\frac{3}{2})] \quad (7)$$

where $N = J - \frac{3}{2}, J - \frac{1}{2}, J + \frac{1}{2}, J + \frac{3}{2}$ and

$$\begin{aligned} T_{A-\frac{3}{2}}^a &= -\frac{3}{2}AA + B[J(J+1) - A(A-3) - \frac{3}{4}] \\ T_{A-\frac{1}{2}}^a &= -\frac{1}{2}AA + B[J(J+1) - A(A-1) + \frac{13}{4}] \\ T_{A+\frac{1}{2}}^a &= +\frac{1}{2}AA + B[J(J+1) - A(A+1) + \frac{13}{4}] \\ T_{A+\frac{3}{2}}^a &= +\frac{3}{2}AA + B[J(J+1) - A(A+3) - \frac{3}{4}] \end{aligned} \quad (8)$$

In the applications of (4) it becomes necessary once more to apply various corrections. Among these, the centrifugal term should be mentioned first. Its case *a* form and the appropriate perturbation-matrix elements are, by (2.1.1-2a, b, c),

$$\begin{aligned} H_{A-\frac{3}{2},A-\frac{3}{2}}^c &= -D\{[J(J+1) - (A-\frac{1}{2})(A-\frac{5}{2})]^2 + 4[J(J+1) - (A-\frac{1}{2})(A-\frac{3}{2})] + (A+\frac{1}{4})\} \\ H_{A-\frac{1}{2},A-\frac{1}{2}}^c &= -D\{[J(J+1) - (A+\frac{1}{2})(A-\frac{3}{2})]^2 + 12[J(J+1) - (A+\frac{1}{2})(A-\frac{3}{2})] - (A+\frac{1}{4})\} \end{aligned} \quad (9)$$

$$H_{A+\frac{1}{2},A+\frac{1}{2}}^c = -D\{[J(J+1) - (A-\frac{1}{2})(A+\frac{3}{2})]^2 + 12[J(J+1) - (A-\frac{1}{2})(A+\frac{3}{2})] + (A+\frac{1}{4})\}$$

$$H_{A+\frac{3}{2},A+\frac{3}{2}}^c = -D\{[J(J+1) - (A+\frac{1}{2})(A+\frac{5}{2})]^2 + 4[J(J+1) - (A+\frac{1}{2})(A+\frac{3}{2})] - (A+\frac{1}{4})\}$$

$$H_{A-\frac{3}{2},A-\frac{1}{2}}^c = -2D[J(J+1) - (A-\frac{5}{2})(A+\frac{1}{2})] \sqrt{3(J-A+\frac{3}{2})(J+A-\frac{1}{2})}$$

$$H_{A-\frac{1}{2},A+\frac{1}{2}}^c = -4D[J(J+1) + 1 - (A-\frac{3}{2})(A+\frac{3}{2})] \sqrt{(J-A+\frac{1}{2})(J+A+\frac{1}{2})} \quad (10)$$

$$H_{A+\frac{1}{2},A+\frac{3}{2}}^c = -2D[J(J+1) - (A-\frac{1}{2})(A+\frac{5}{2})] \sqrt{3(J-A-\frac{1}{2})(J+A+\frac{3}{2})}$$

$$H_{\Lambda-3/2, \Lambda+1/2}^c = -2D \sqrt{3(J-\Lambda+1/2)(J-\Lambda+3/2)(J+\Lambda-1/2)(J+\Lambda+1/2)}$$

$$H_{\Lambda-1/2, \Lambda+3/2}^c = -2D \sqrt{3(J-\Lambda-1/2)(J-\Lambda+1/2)(J+\Lambda+1/2)(J+\Lambda+3/2)}$$

Similarly as in the case of the triplet terms, formulas (9), (10) and (7) yield the intermediate form of the centrifugal correction according to (1.5-15) as

$$\begin{aligned} H_N^c(J) = & S_{\Lambda+3/2, N}^2 H_{\Lambda+3/2, \Lambda+3/2}^c + S_{\Lambda+1/2, N}^2 H_{\Lambda+1/2, \Lambda+1/2}^c + S_{\Lambda-1/2, N}^2 H_{\Lambda-1/2, \Lambda-1/2}^c + \\ & + S_{\Lambda-3/2, N}^2 H_{\Lambda-3/2, \Lambda-3/2}^c + 2S_{\Lambda+3/2, N} S_{\Lambda+1/2, N} H_{\Lambda+3/2, \Lambda+1/2}^c + \\ & + 2S_{\Lambda+1/2, N} S_{\Lambda-1/2, N} H_{\Lambda+1/2, \Lambda-1/2}^c + 2S_{\Lambda-1/2, N} S_{\Lambda-3/2, N} H_{\Lambda-1/2, \Lambda-3/2}^c + \\ & + 2S_{\Lambda+3/2, N} S_{\Lambda-1/2, N} H_{\Lambda+3/2, \Lambda-1/2}^c + 2S_{\Lambda+1/2, N} S_{\Lambda-3/2, N} H_{\Lambda+1/2, \Lambda-3/2}^c \end{aligned} \quad (11)$$

where $N = J - 3/2, J - 1/2, J + 1/2, J + 3/2$. Since (7) is somewhat complicated, (11) is none too simple, either: its use is to be recommended only when D , compared with B , is greater than usual. If the term lies close to case a , then the diagonal elements of (9), i.e. of the case a matrix can be used. In the case of higher rotational quantum numbers the case b form of the centrifugal term (2.1.1-6) can be applied. It is to be noted that (11) also reduces to (2.1.1-6) on the substitution of $Y = 0$.

As a further correction, the elements of the spin-spin interaction should also be taken into account because, in the quartet case, there are at least three electrons outside the closed shell. The case a form of this interaction is given by (2.1.1-3a) on putting $S = 3/2$ and $\Sigma = -3/2, -1/2, +1/2, +3/2$. The correction element of the spin-spin interaction, derived for the intermediate case by the procedure from (1.5-11) to (1.5-15) making use of the transformation-matrix elements (7), is the following (Kovács [104]):

$$H_N^{ss}(J) = 3\varepsilon - 6\varepsilon[S_{\Lambda+1/2, N}^2 + S_{\Lambda-1/2, N}^2] \quad (12)$$

where $N = J - 3/2, J - 1/2, J + 1/2, J + 3/2$. In a manner similar to that for the triplet terms, it is practical to incorporate the first term on the right-hand side in v_0 , since only the coefficient of the second term can be determined from the experimental data, and, as it will be seen later, this latter coefficient is also modified by the higher-order perturbations due to spin-orbit interaction. Putting $Y = 0$ in the transformation-matrix elements in (12) yields the case b form of the spin-spin interaction; it is the same as (2.1.1-7a) with $S = 3/2$.

The interaction between rotation and spin should again be corrected for. The case b form of this correction is again given by (2.1.1-8), whereas to find the intermediate form the case a matrix is to be rewritten by

(2.1.1-4a, b) as follows:

$$\begin{aligned}
 H_{A-3/2, A-3/2}^{sr} &= H_{A+3/2, A+3/2}^{sr} = -\frac{3}{2}\gamma \\
 H_{A-1/2, A-1/2}^{sr} &= H_{A+1/2, A+1/2}^{sr} = -\frac{7}{2}\gamma \\
 H_{A-3/2, A-1/2}^{sr} &= H_{A-1/2, A-3/2}^{sr} = -\frac{1}{2}\gamma \sqrt{3(J+A-1/2)(J-A+3/2)} \\
 H_{A-1/2, A+1/2}^{sr} &= H_{A+1/2, A-1/2}^{sr} = -\gamma \sqrt{(J+A+1/2)(J-A+1/2)} \\
 H_{A+1/2, A+3/2}^{sr} &= H_{A+3/2, A+1/2}^{sr} = -\frac{1}{2}\gamma \sqrt{3(J+A+3/2)(J-A-1/2)}
 \end{aligned} \quad (13)$$

By (13), (7) and (1.5-15), the intermediate form then becomes

$$\begin{aligned}
 H_N^{ss}(J) = & -\frac{\gamma}{2} \left[3 + 4(S_{A+1/2, N}^2 + S_{A-1/2, N}^2) + \right. \\
 & + 2S_{A+3/2, N}S_{A+1/2, N} \sqrt{3(J+A+3/2)(J-A-1/2)} + \\
 & + 4S_{A+1/2, N}S_{A-1/2, N} \sqrt{(J+A+1/2)(J-A+1/2)} + \\
 & \left. + 2S_{A-1/2, N}S_{A-3/2, N} \sqrt{3(J+A-1/2)(J-A+3/2)} \right]
 \end{aligned} \quad (14)$$

where again $N = J - 3/2, J - 1/2, J + 1/2, J + 3/2$. Formula (14) reduces to (2.1.1-8) on the substitution $Y = 0$, whereas for $Y \rightarrow \infty$ it yields the diagonal elements of (13), i.e. the expression (2.1.1-4a). In view of the above considerations the full term formula will be

$$F_N(J) = T_N(J) + H_N^c(J) + H_N^{ss}(J) + H_N^{sr}(J) \quad (15)$$

where $N = J - 3/2, J - 1/2, J + 1/2, J + 3/2$.

⁴ Σ Terms. Putting $A = 0$ and $Y = 0$ in Formula (15) yields the following term formulas for the ⁴ Σ terms:

$$\begin{aligned}
 F_{J-3/2}(N) &= F_1(N) = v_0 + B_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 - \\
 &\quad - 3\varepsilon \frac{N}{2N+3} + \frac{3}{2}\gamma N
 \end{aligned}$$

$$\begin{aligned}
 F_{J-1/2}(N) &= F_2(N) = v_0 + B_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 + \\
 &\quad + 3\varepsilon \frac{N+3}{2N+3} + \frac{1}{2}\gamma(N-3)
 \end{aligned}$$

$$\begin{aligned}
 F_{J+1/2}(N) &= F_3(N) = v_0 + B_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 + \\
 &\quad + 3\varepsilon \frac{N-1}{2N-1} - 1/2\gamma(N+4) \\
 F_{J+3/2}(N) &= F_4(N) = v_0 + B_\Sigma N(N+1) - D_\Sigma N^2(N+1)^2 - \\
 &\quad - 3\varepsilon \frac{N+1}{2N-1} - 3/2\gamma(N+1)
 \end{aligned} \tag{16}$$

These formulas were first given by Budó [21] who also derived some more rigorous, analytically closed formulas. Adding the case a form of (12) to the diagonal terms of the original secular determinant, we obtain in the case of the $^4\Sigma$ terms two easily manageable second-order equations, whose roots are:

$$\begin{aligned}
 T_{J-3/2}(N) &= v_0 + B_\Sigma \left[N(N+1) + (2N+3) - \right. \\
 &\quad \left. - \sqrt{9 \left(\frac{\varepsilon}{B_\Sigma} \right)^2 + 6 \frac{\varepsilon}{B_\Sigma} N + (2N+3)^2} \right] \\
 T_{J-1/2}(N) &= v_0 + B_\Sigma \left[N(N+1) + (2N+3) - \right. \\
 &\quad \left. - \sqrt{9 \left(\frac{\varepsilon}{B_\Sigma} \right)^2 - 6 \frac{\varepsilon}{B_\Sigma} (N+3) + (2N+3)^2} \right] \\
 T_{J+1/2}(N) &= v_0 + B_\Sigma \left[N(N+1) - (2N-1) + \right. \\
 &\quad \left. + \sqrt{9 \left(\frac{\varepsilon}{B_\Sigma} \right)^2 + 6 \frac{\varepsilon}{B_\Sigma} (N-2) + (2N-1)^2} \right] \\
 T_{J+3/2}(N) &= v_0 + B_\Sigma \left[N(N+1) - (2N-1) + \right. \\
 &\quad \left. + \sqrt{9 \left(\frac{\varepsilon}{B_\Sigma} \right)^2 - 6 \frac{\varepsilon}{B_\Sigma} (N+1) + (2N-1)^2} \right]
 \end{aligned} \tag{17}$$

Similarly as in the triplet case, more rigorous expressions can be obtained for the spin-rotation interaction and for the centrifugal term, if ϵ , the coefficient of the spin-spin interaction, compared with the coefficients of the above interactions, is great. By the procedure from (1.5-11) to (1.5-15) the expressions of the above interactions can be calculated from (11) and (14), with the difference that to calculate the transformation-matrix elements S figuring in those formulas we now use instead of (7) the expressions:

$$\begin{aligned}
 s_{-3/2,N} &= 2\sqrt{3(J - 1/2)(J + 1/2)^2(J + 3/2)} C_N(J) \\
 s_{-1/2,N} &= -2(J + 1/2) C_N(J)^2 \\
 s_{+1/2,N} &= C_N(J) \left\{ C_N(J) \left[C_N(J) + 4 - 6 \frac{\epsilon}{B_\Sigma} \right] - 3(J - 1/2)(J + 3/2) \right\} \\
 s_{+3/2,N} &= -\sqrt{3(J - 1/2)(J + 3/2)} \left\{ C_N(J) \left[C_N(J) + 4 - 6 \frac{\epsilon}{B_\Sigma} \right] - \right. \\
 &\quad \left. - 3(J - 1/2)(J + 3/2) \right\}
 \end{aligned} \tag{17a}$$

where

$$\begin{aligned}
 C_{J-3/2}(J) &= J - 3/2 + 3 \frac{\epsilon}{B_\Sigma} + \sqrt{9 \left(\frac{\epsilon}{B_\Sigma} \right)^2 + 3 \frac{\epsilon}{B_\Sigma} (2J - 3) + 4J^2} \\
 C_{J-1/2}(J) &= -J - 5/2 + 3 \frac{\epsilon}{B_\Sigma} + \sqrt{9 \left(\frac{\epsilon}{B_\Sigma} \right)^2 - 3 \frac{\epsilon}{B_\Sigma} (2J + 5) + 4(J + 1)^2} \\
 C_{J+1/2}(J) &= -J - 5/2 + 3 \frac{\epsilon}{B_\Sigma} - \sqrt{9 \left(\frac{\epsilon}{B_\Sigma} \right)^2 - 3 \frac{\epsilon}{B_\Sigma} (2J + 5) + 4(J + 1)^2} \\
 C_{J+3/2}(J) &= J - 3/2 + 3 \frac{\epsilon}{B_\Sigma} - \sqrt{9 \left(\frac{\epsilon}{B_\Sigma} \right)^2 + 3 \frac{\epsilon}{B_\Sigma} (2J - 3) + 4J^2}
 \end{aligned} \tag{17b}$$

Nevin [163] was the first to analyse a $^4\Sigma^-$ state in the O_2^+ molecule, which could be described sufficiently even by Formula (16). Figure 2.13 shows the quartet splitting calculated by Formula (16), and the relevant experimental results.

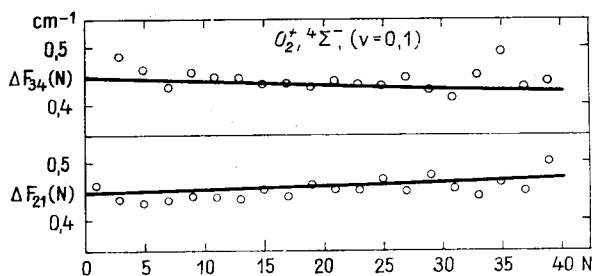


Fig. 2.13 The average of the spin splittings found at the $v=0$ and 1 levels of $^4\Sigma^-$, in the O_2^+ molecule, according to Nevin [163]. In the expressions of F_2-F_1 and F_3-F_4 , calculated from Equation (16) of the theoretical curve, $\varepsilon = 0.1487 \text{ cm}^{-1}$ and $\gamma = -0.00066 \text{ cm}^{-1}$.

Perturbation by the farther-lying terms modifies (16), but—similarly as in the cases discussed so far—it alters only the constants and leaves the dependence on the rotational quantum number unchanged. For the case of perturbation by the $^4\Pi$ terms, the modified constants were given by Budó and Kovács [26] as

$$B_{\Sigma'} = B_{\Sigma} + 8 \sum' \frac{|\eta|^2}{\nu}; \quad \varepsilon' = \varepsilon - \frac{2}{27} \sum' \frac{|\xi|^2}{\nu}; \quad \gamma' = \gamma - \frac{2}{3} \sum' \frac{\xi\eta^* + \xi^*\eta}{\nu} \quad (18)$$

where ξ , η and ν have meanings similar to those given previously.

If one of these $^4\Pi$ terms is sufficiently close to the $^4\Sigma$ term, the constants are modified further: correction terms depending on the rotational quantum number appear and deviations from (16) occur. These are given below according to Kovács [113]:

$$\begin{aligned} \Delta F_1(N) &= -[3\sigma(N+1) - \tau]N^2 \\ \Delta F_2(N) &= -[\sigma(N-3)(N+1) + \tau(N+3)]N \\ \Delta F_3(N) &= +[\sigma N(N+4) - \tau(N-2)](N+1) \\ \Delta F_4(N) &= +[3\sigma N + \tau](N+1)^2 \end{aligned} \quad (19)$$

where

$$\Delta F_i(N) = F'_i(N) - \overline{F_i(N)}; \quad \sigma = 2 \frac{\xi\eta^* + \xi^*\eta}{\nu^2} (B_{\Pi} - B_{\Sigma}); \quad \tau = \frac{|\xi|^2}{\nu^2} (B_{\Pi} - B_{\Sigma}) \quad (20)$$

$F'_i(N)$ means here the perturbed (i.e. the observed) term values, whereas $\overline{F_i(N)}$ is formally identical with (16), except for the constants.

Besides the $^4\Pi$ terms, the states $^2\Sigma$, $^2\Pi$ and $^4\Sigma$ can also perturb the $^4\Sigma$ terms (the terms of higher multiplicity are negligible). This perturbation results in a constant shift which affects the constant ε of the spin-spin interaction, while B and γ remain unchanged.

In addition to the previously mentioned O_2^+ molecule, Kleman and Werhagen [92] found a quartet transition also in the GeH molecule. The $^4\Sigma$ term involved in this transition also shows a deviation from (16) but, owing to the insufficiency of experimental data, it cannot be decided whether or not the deviations observed can be interpreted by (19). Furthermore, Verma [210] analysed a $^4\Sigma$ state of the SiF molecule, which deviated from Formula (16); the discrepancy could not be interpreted by (19). Hougen [80] attempted a different theoretical interpretation of these deviations, but without much success.

$^4\Pi$ and $^4\Delta$ Terms. Putting $\Lambda = 1$ and $\Lambda = 2$ in (15) we obtain the term formulas of the terms $^4\Pi$ and $^4\Delta$, respectively. The fine structure of the $^4\Pi$ term has not been analyzed so far; for the $^4\Pi$ term, the only report on hand is the one by Nevin [163] concerning the O_2^+ molecule. Nevin found Formula

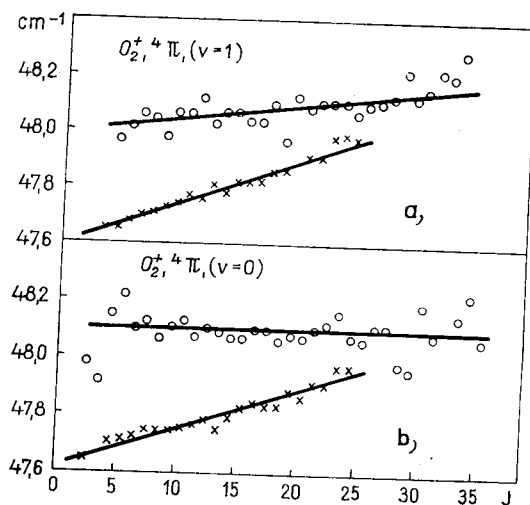


Fig. 2.14 The coupling constant A at the levels $v = 1$ (a) and $v = 0$ (b) of the $^4\Pi$ term in the O_2^+ molecule, vs. the rotational quantum number. The small circles are calculated from $\Delta F_{32}(J)$, the crosses from $\Delta F_{41}(J)$. On taking into account the spin-orbit interaction, the change in A with the rotational quantum number disappears and $A = -47.792 \text{ cm}^{-1}$.

(4) to yield a certain discrepancy, in that the coupling constant A calculated therefrom apparently 'changed' with the rotational quantum number and, what is more, it assumed different values, according as it was calculated from $\Delta F_{32}(J)$ or $\Delta F_{41}(J)$ (Fig. 2.14). The reason for this subsequently turned out to be that the correction (12) was not applied so that the spin-spin interaction and the closely related spin-orbit interaction (to be discussed below) were left out of consideration.

The spin-orbit interaction leads to a perturbation of the $^4\Pi$ terms by the $^2\Pi$ terms and of the $^4\Delta$ terms by the $^2\Delta$ terms, respectively; according to Budó and Kovács [28] and Kovács [104] these effects modify (12) as follows:

$$H_N^{ss,so}(J) = 3\varepsilon - \beta [S_{A+1/2,N}^2 + S_{A-1/2,N}^2] \quad (21)$$

where

$$\beta = 6\varepsilon - \sum_v \frac{|\mathbf{q}|^2}{v} \quad (22)$$

and ϱ is the matrix element of the spin-orbit interaction between the $^4\Pi$ and $^2\Pi$ terms or the $^4\Delta$ and $^2\Delta$ terms, respectively; ν is the term spacing between the corresponding quartet and doublet terms. Let us now denote the sum of the first, second and fourth terms of (15) by $F_N^*(J)$ and let $F_N(J) = F_N^*(J) + H_N^{ss,so}(J)$. Then the deviation in the quartet splitting resulting from the spin-spin and spin-orbit interactions will have the form

$$\Delta F_{N,N-1}(J) - \Delta F_{N,N-1}^*(J) = \beta[S_{A+1/2,N-1}^2 + S_{A-1/2,N-1}^2 - S_{A+1/2,N}^2 - S_{A-1/2,N}^2] \quad (23)$$

where $N = J + 3/2, J + 1/2, J - 1/2$.

Budó and Kovács [28], and later Kovács and Weniger [130] used expression (23) to interpret the apparently anomalous multiplet splittings found at the vibrational

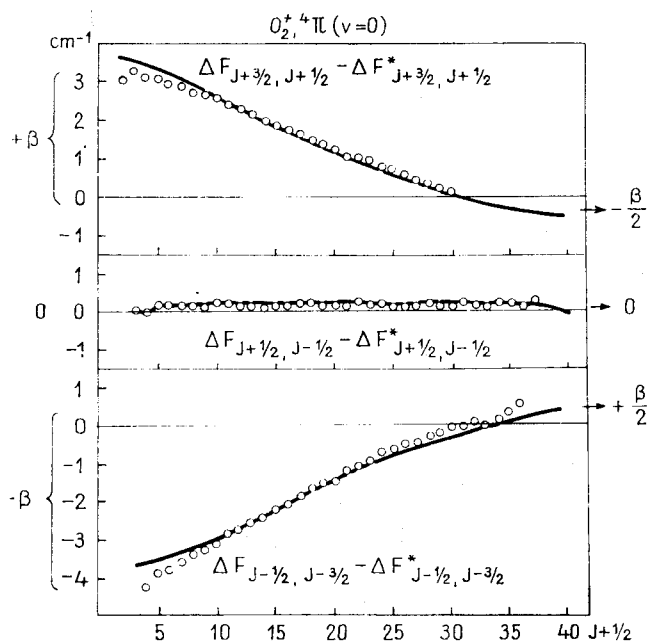


Fig. 2.15 Deviations from the spin-splittings calculated by formula (4) at the $v = 0$ level of $^4\Pi$, in the O_2^+ molecule, according to Budó and Kovács [28]. In Equation (23) of the theoretical curves, calculated with regard to the spin-orbit interaction, $\beta = 3.712 \text{ cm}^{-1}$. Similar figures can be obtained for the levels $v = 1, 2, 3, 4, 5, 6$ (Kovács and Weniger [130]).

levels $v = 0, 1, 2, 3, 4, 5, 6$ of the O_2^+ molecule, as revealed by the experimental data of Nevin [163, 164] and Weniger [218] (see also [116] and [119]). In Fig. 2.15 the deviations found experimentally are plotted against those calculated by (23) at the level $v = 0$. Agreement at the other levels is similarly good.

Application of (23) makes the coupling constant A strictly independent of the rotational quantum number; moreover, now A is found to be the same whether calculated from $\Delta F_{32}(J)$ or from $\Delta F_{41}(J)$ ($A = -47.792 \text{ cm}^{-1}$).

(b) Λ -Type Doubling. In the case of the ${}^4\Pi$ terms the farther-lying ${}^4\Sigma$ and ${}^2\Sigma$ terms do not equally perturb the twofold degenerate components of the ${}^4\Pi$ term, but, depending on the symmetry of the perturbing Σ term, they affect either the one or the other component more strongly. The otherwise coinciding levels are therefore split up and Λ -type doubling occurs.

Using for the splitting of the individual terms the method already described with respect to the triplet case, Budó and Kovács [25] found

$$\begin{aligned} \Delta v({}^4\Pi_N) = & C_0 S_{1/2,N} S_{-1/2,N} + C_1 [S_{3/2,N} S_{-1/2,N} \sqrt{3(J - 1/2)(J + 3/2)} + \\ & + S_{1/2,N}^2 (J + 1/2)] + 2C_2 [S_{5/2,N} S_{-1/2,N} \sqrt{(J - 3/2)(J - 1/2)(J + 3/2)(J + 5/2)} \\ & + S_{3/2,N} S_{1/2,N} (J + 1/2) \sqrt{(J - 1/2)(J + 3/2)}] \end{aligned} \quad (24)$$

where $N = J - 3/2, J - 1/2, J + 1/2, J + 3/2$; the values of the quantities S are to be taken from (7) and

$$\begin{aligned} C_0 = 2\sqrt{3} \left[\sum (-1)^x \frac{|\xi|^2}{v} - \frac{1}{9} \sum (-1)^{x'} \frac{|\xi'|^2}{v'} \right]; \quad C_1 = 4 \sum (-1)^x \frac{\xi \eta^* + \xi^* \eta}{v} \\ C_2 = 8 \sum (-1)^x \frac{|\eta|^2}{v} \end{aligned} \quad (25)$$

$$\xi = \frac{2\xi}{3} + 4\eta; \quad \eta = (BL_\xi)({}^4\Pi; {}^4\Sigma_k); \quad \xi = (\Sigma a_i l_{i\xi})({}^4\Pi; {}^4\Sigma_k); \quad \xi' = (\Sigma a_i l_{i\xi})({}^4\Pi; {}^2\Sigma_k)$$

furthermore, Σ and Σ' in the exponent are 0 or 1, according as the Σ state in question is a Σ^+ or Σ^- .

As is shown in Fig. 2.16, the application of formula (24) to the Λ -type doubling of the ${}^4\Pi$ term of the O_2^+ molecule gives a result in excellent agreement with the experimental data (Budó and Kovács [25]).

In *Hund's case a* the substitution $Y \rightarrow \infty$ leads by (24) to

$$\begin{aligned} \Delta v({}^4\Pi_{5/2}) &= 0 \\ \Delta v({}^4\Pi_{3/2}) &= 0 \\ \Delta v({}^4\Pi_{1/2}) &= C_1 (J + 1/2) \\ \Delta v({}^4\Pi_{-1/2}) &= 0 \end{aligned} \quad (26)$$

An approximation of higher order yields some weak splittings, they are directly proportional to the fifth power of the rotational quantum number but inversely proportional to the third power of Y in the case of $\Delta v({}^4\Pi_{5/2})$; in the case of $\Delta v({}^4\Pi_{3/2})$ they are directly proportional to the third power of J and inversely proportional to Y ; and finally, for $\Delta v({}^4\Pi_{-1/2})$ they are directly proportional to the rotational quantum number and inversely proportional to Y (Budó and Kovács [25]).

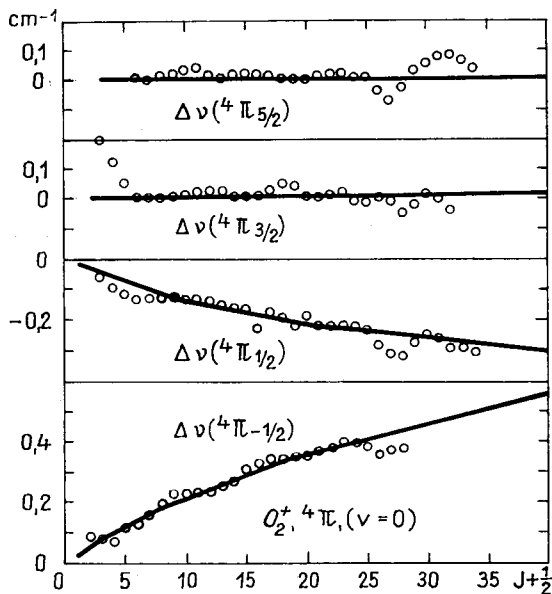


Fig. 2.16 *A*-type doubling observed at the $v=0$ level of ${}^4\Pi$, in the O_2^+ molecule, according to Budó and Kovács [25]. In Eq. (24) of the theoretical curve, $C_0 = 0.58 \text{ cm}^{-1}$, $C_1 = 0.0077 \text{ cm}^{-1}$, $C_2 = 0.0001 \text{ cm}^{-1}$.

In *Hund's case b* the substitution $Y = 0$ yields

$$\begin{aligned}
 \Delta v({}^4\Pi_{J-3/2}) &= + \left[\frac{\sqrt{3}}{8} C_0 - \frac{3}{4} C_1 + \frac{3}{2} C_2 \right] \frac{2N}{2N+3} - \\
 &\quad - \left[\frac{3}{4} C_1 - C_2 \right] N + C_2 N(N+1) \\
 \Delta v({}^4\Pi_{J-1/2}) &= - \left[\frac{\sqrt{3}}{8} C_0 - \frac{3}{4} C_1 + \frac{3}{2} C_2 \right] \frac{2(N+3)}{2N+3} - \\
 &\quad - \frac{1}{3} \left[\frac{3}{4} C_1 - C_2 \right] (N-3) + C_2 N(N+1) \\
 \Delta v({}^4\Pi_{J+1/2}) &= - \left[\frac{\sqrt{3}}{8} C_0 - \frac{3}{4} C_1 + \frac{3}{2} C_2 \right] \frac{2(N-2)}{2N-1} + \\
 &\quad + \frac{1}{3} \left[\frac{3}{4} C_1 - C_2 \right] (N+4) + C_2 N(N+1) \\
 \Delta v({}^4\Pi_{J+3/2}) &= + \left[\frac{\sqrt{3}}{8} C_0 - \frac{3}{4} C_1 + \frac{3}{2} C_2 \right] \frac{2(N+1)}{2N-1} + \\
 &\quad + \left[\frac{3}{4} C_1 - C_2 \right] (N+1) + C_2 N(N+1)
 \end{aligned} \tag{27}$$

Similarly as in the previous cases, it again appears as if the *A*-type doubling were due to slight changes in the constants of the case *b* terms.



2.1.6. Quintet Terms

(a) **General Theory of Spin Splitting.** The procedure resorted to until now, i.e. the appropriate modification of *Hund's* case *a* leads to time-consuming calculations for terms of multiplicity higher than quartets; the formulas so derived are complicated and difficult to use in practice. Starting, however, from *Hund's* case *b*, there can be derived even for terms of higher multiplicity relatively simple formulas which probably are in reasonably good agreement with experiments for higher values of the rotational quantum number, provided Y is not too great. Starting therefore from the case *b* energies and perturbation-matrix elements given in (2.1.1-5a, b) we obtain in the present case a secular equation of fifth degree whose approximate solutions were given by Rao [186] as

$$\begin{aligned} T_{J-2}(N) &= v_0 + B \left[N(N+1) - A^2 + \frac{2YA^2}{N+1} + \varphi_{J-2}(N) \right] \\ T_{J-1}(N) &= v_0 + B \left[N(N+1) - A^2 + \frac{YA^2(N-2)}{N(N+1)} + \varphi_{J-1}(N) \right] \\ T_J(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{3YA^2}{N(N+1)} + \varphi_J(N) \right] \\ T_{J+1}(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{YA^2(N+3)}{N(N+1)} - \varphi_{J+1}(N) \right] \\ T_{J+2}(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{2YA^2}{N} - \varphi_{J+2}(N) \right] \end{aligned} \quad (1)$$

where

$$\begin{aligned} \varphi_{J-2}(N) &= 2A^2Y^2 \frac{(N+2)(N+3)[(N+1)^2 - A^2]}{(N+1)(2N+3)[YA^2(N+5) - 2(N+1)^2(N+2)]} \\ \varphi_{J-1}(N) &= 3A^2Y^2 \times \\ &\times \frac{N^2(N+2)(2N+5)[(N+1)^2 - A^2]}{(N+1)(2N+1)(2N+3)[YA^2(N-1)(N+4) - 2N(N+1)^2(N+2)]} \\ &\quad - \varphi_{J-2}(N-1) \\ \varphi_J(N) &= (\varphi_{J+2}(N+2) + \varphi_{J+1}(N+1)) - (\varphi_{J-1}(N-1) + \varphi_{J-2}(N-2)) \\ \varphi_{J+1}(N) &= 3A^2Y^2 \frac{(N-1)(N+1)^2(2N-3)[N^2 - A^2]}{N(2N-1)(2N+1)[YA^2(N-3)(N+2) - 2(N-1)N^2(N+1)]} \\ &\quad - \varphi_{J+2}(N+1) \\ \varphi_{J+2}(N) &= 2A^2Y^2 \frac{(N-2)(N-1)[N^2 - A^2]}{N(2N-1)[YA^2(N-4) - 2(N-1)^2N]} \end{aligned} \quad (2)$$

Without the knowledge of the transformation matrix it is not possible to give the intermediate forms of the centrifugal correction, and of the corrections for the spin-spin and spin-rotation interactions. Thus it is best to take them in their case b forms, i.e. according to (2.1.1-6), (2.1.1-7a, b), (2.1.1-8), all the more so since formulas (1) give a sufficient approximation only in the neighbourhood of case b . The full term formulas will then be

$$F_i(N) = T_i(N) + H_i^e(N) + H_i^{ss}(N) + H_i^{sr}(N) \quad (3)$$

where $i = J - 2, J - 1, J, J + 1, J + 2$, and

$$H_i^e(N) = -D[N(N + 1) - \Lambda^2]^2$$

furthermore,

$$H_{J-2}^{ss}(N) + H_{J-2}^{sr}(N) = -6\varepsilon \frac{N}{2N + 3} \Phi^\mp(N) + 2\gamma N \sigma(N)$$

$$H_{J-1}^{ss}(N) + H_{J-1}^{sr}(N) = 3\varepsilon \frac{N + 6}{2N + 3} \Phi^\mp(N) + \gamma(N - 2)\sigma(N) \quad (4)$$

$$H_J^{ss}(N) + H_J^{sr}(N) = 3\varepsilon \left(1 + \frac{3}{2N + 3} - \frac{3}{2N - 1} \right) \Phi^\mp(N) - 3\gamma\sigma(N)$$

$$H_{J+1}^{ss}(N) + H_{J+1}^{sr}(N) = 3\varepsilon \frac{N - 5}{2N - 1} \Phi^\mp(N) - \gamma(N + 3)\sigma(N)$$

$$H_{J+2}^{ss}(N) + H_{J+2}^{sr}(N) = -6\varepsilon \frac{N + 1}{2N - 1} \Phi^\mp(N) - 2\gamma(N + 1)\sigma(N)$$

where

$$\Phi^\mp(N) = 1 - \frac{3\Lambda^2}{N(N + 1)} \mp \frac{1}{2} \frac{\alpha}{\varepsilon} \delta_{\Lambda, \pm 1}; \quad \sigma(N) = 1 - \frac{\Lambda^2}{N(N + 1)} \quad (5)$$

${}^3\Sigma$ Terms. The formulas for the ${}^3\Sigma$ terms can be obtained from (3) by putting $\Lambda = 0$. Then

$$F_i(N) = v_0 + BN(N + 1) - DN^2(N + 1)^2 + H_i^{ss}(N) + H_i^{sr}(N) \quad (6)$$

where $i = J - 2, \dots, J + 2$. The last two terms are easily obtained from (4) by putting $\Phi^\mp(N) = \sigma(N) = 1$. These formulas were also given by Rao [185].

In the case of perturbation by farther-lying terms the ${}^3\Sigma$ terms behave in a manner similar to those of lower multiplicity: i.e. there is no change in the dependence on the rotational quantum number; only the constants are affected. If, however, one

of the 3H terms comes sufficiently close to the ${}^3\Sigma$ term in question, the following deviations from (6) result (Kovács [113]):

$$\begin{aligned} \Delta F_1(N) &= -[\sigma(2N+3)(N+1) - 2\tau(2N+1)]N \\ \Delta F_2(N) &= -[\sigma(N+1)^2 - \tau(N-4)]N \\ \Delta F_3(N) &= 0 \\ \Delta F_4(N) &= +[\sigma N^2 + \tau(N+5)](N+1) \\ \Delta F_5(N) &= +[\sigma(2N-1)N + 2\tau(2N+1)](N+1) \end{aligned} \quad (7)$$

where the suffixes 1, ..., 5 serve as a shorthand notation for $J-2, \dots, J+2$. The two constants in the formulas above are:

$$\sigma = 4(B_{II} - B_{\Sigma}) \frac{\xi\eta^* + \xi^*\eta}{v^2}; \quad \tau = (B_{II} - B_{\Sigma}) \frac{|\xi|^2}{v^2} \quad (8)$$

where ξ and η have meanings similar to those given previously.

The fine structure of quintet terms has not been analysed so far.

(b) Λ -Type Doubling. Since the elements of the transformation matrix are not known, the Λ -type splitting cannot be given for the intermediate case either. Some splitting appears in the term formulas proper as a result of the spin-spin interaction. The spin-orbit interaction provides a further contribution which in case b is of the form

$$\begin{aligned} \Delta v({}^5H_{J-2}) &= +\frac{2}{3}\alpha_0 \frac{N}{2N+3} - \alpha_1 N + \alpha_2 N(N+1) \\ \Delta v({}^5H_{J-1}) &= -\frac{1}{3}\alpha_0 \frac{N+6}{2N+3} - \frac{1}{2}\alpha_1(N-2) + \alpha_2 N(N+1) \\ \Delta v({}^5H_J) &= -\frac{1}{3}\alpha_0 \left(1 + \frac{2}{2N+3} - \frac{2}{2N-1}\right) + \frac{3}{2}\alpha_1 + \alpha_2 N(N+1) \quad (9) \\ \Delta v({}^5H_{J+1}) &= -\frac{1}{3}\alpha_0 \frac{N-5}{2N-1} + \frac{1}{2}\alpha_1(N+3) + \alpha_2 N(N+1) \\ \Delta v({}^5H_{J+2}) &= +\frac{2}{3}\alpha_0 \frac{N+1}{2N-1} + \alpha_1(N+1) + \alpha_2 N(N+1) \end{aligned}$$

where

$$\alpha_0 = \sum (-1)^x \frac{|\xi|^2}{v} + 9\alpha; \quad \alpha_1 = 2 \sum (-1)^x \frac{\xi\eta^* + \xi^*\eta}{v}; \quad \alpha_2 = 8 \sum (-1)^x \frac{|\eta|^2}{v} \quad (10)$$

Formulas (9) and (10) have not as yet been applied in practice.

2.1.7. *Sextet Terms*

(a) General Theory of Spin Splitting. Starting from *Hund's case b*, the procedure described previously yields for the neighbourhood of case *b* the formulas (Rao [185]):

$$\begin{aligned}
 T_{J-5/2}(N) &= v_0 + B \left[N(N+1) - A^2 + \frac{5YA^2}{2(N+1)} + \varphi_{J-5/2}(N) \right] \\
 T_{J-3/2}(N) &= v_0 + B \left[N(N+1) - A^2 + \frac{YA^2(3N-5)}{2N(N+1)} + \varphi_{J-3/2}(N) \right] \\
 T_{J-1/2}(N) &= v_0 + B \left[N(N+1) - A^2 + \frac{YA^2(N-4)}{2N(N+1)} + \varphi_{J-1/2}(N) \right] \\
 T_{J+1/2}(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{YA^2(N+9)}{2N(N+1)} - \varphi_{J+1/2}(N) \right] \\
 T_{J+3/2}(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{YA^2(3N+8)}{2N(N+1)} - \varphi_{J+3/2}(N) \right] \\
 T_{J+5/2}(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{5YA^2}{2N} - \varphi_{J+5/2}(N) \right]
 \end{aligned} \quad (1)$$

where

$$\begin{aligned}
 \varphi_{J-5/2}(N) &= \frac{5}{4} A^2 Y^2 \frac{(N+2)(2N+7)[(N+1)^2 - A^2]}{(N+1)(2N+3)[YA^2(N+6) - 2(N+1)^2(N+2)]} \\
 \varphi_{J-3/2}(N) &= 8A^2 Y^2 \times \\
 &\times \frac{N^2(N+2)(N+3)[(N+1)^2 - A^2]}{(N+1)(2N+1)(2N+3)[YA^2(N-1)(N+5) - 2N(N+1)^2(N+2)]} \\
 &\quad - \varphi_{J-5/2}(N-1) \\
 \varphi_{J-1/2}(N) &= \frac{9}{8} A^2 Y^2 \frac{N(N+2)(2N-1)(2N+5)[(N+1)^2 - A^2]}{(N+1)^2(2N+1)(2N+3)[4YA^2 - N(N+1)(N+2)]} \\
 &\quad - \varphi_{J-3/2}(N-1) - \varphi_{J-5/2}(N-2) \\
 \varphi_{J+1/2}(N) &= \frac{9}{8} A^2 Y^2 \frac{(N-1)(N+1)(2N-3)(2N+3)[N^2 - A^2]}{N^2(2N-1)(2N+1)[4YA^2 - (N-1)N(N+1)]} \\
 &\quad - \varphi_{J+3/2}(N+1) - \varphi_{J+5/2}(N+2)
 \end{aligned} \quad (2)$$

$$\varphi_{J+3/2}(N) = 8A^2 Y^2 \times$$

$$\times \frac{(N-2)(N-1)(N+1)^2 [N^2 - A^2]}{N(2N-1)(2N+1) [YA^2(N-4)(N+2) - 2(N-1)N^2(N+1)] - \varphi_{J+5/2}(N+1)}$$

$$\varphi_{J+5/2}(N) = \frac{5}{4} A^2 Y^2 \frac{(N-1)(2N-5)[N^2 - A^2]}{N(2N-1)(2N-5) [YA^2(N-5) + 2(N-1)N^2]}$$

As in the cases discussed previously, Formula (1) is yet to be complemented with the appropriate correction terms. Then

$$F_i(N) = T_i(N) + H_i^c(N) + H_i^{ss}(N) + H_i^{sr}(N) \quad (3)$$

where $i = J - 5/2, J - 3/2, J - 1/2, J + 1/2, J + 3/2, J + 5/2$; $H_i^c(N)$ is to be taken from (2.1.1-6); and by (2.1.1-7a) and (2.1.1-8) $H_i^{ss}(N) + H_i^{sr}(N)$ will be

$$H_{J-5/2}^{ss}(N) + H_{J-5/2}^{sr}(N) = -10\varepsilon \frac{N}{2N+3} \Phi(N) + \frac{5}{2} \gamma N \sigma(N)$$

$$H_{J-3/2}^{ss}(N) + H_{J-3/2}^{sr}(N) = +\varepsilon \left[1 + \frac{27}{2N+3} \right] \Phi(N) + \frac{\gamma}{2} (3N-5) \sigma(N)$$

$$H_{J-1/2}^{ss}(N) + H_{J-1/2}^{sr}(N) = +\varepsilon \left[4 + \frac{27}{2N+3} - \frac{15}{2N-1} \right] \Phi(N) +$$

$$+ \frac{\gamma}{2} (N-8) \sigma(N) \quad (4)$$

$$H_{J+1/2}^{ss}(N) + H_{J+1/2}^{sr}(N) = +\varepsilon \left[4 + \frac{15}{2N+3} - \frac{27}{2N-1} \right] \Phi(N) -$$

$$- \frac{\gamma}{2} (N+9) \sigma(N)$$

$$H_{J+3/2}^{ss}(N) + H_{J+3/2}^{sr}(N) = +\varepsilon \left[1 - \frac{27}{2N-1} \right] \Phi(N) - \frac{\gamma}{2} (3N+8) \sigma(N)$$

$$H_{J+5/2}^{ss}(N) + H_{J+5/2}^{sr}(N) = -10\varepsilon \frac{N+1}{2N-1} \Phi(N) - \frac{5}{2} \gamma (N+1) \sigma(N)$$

where

$$\Phi(N) = 1 - \frac{3A^2}{N(N+1)}; \quad \sigma(N) = 1 - \frac{A^2}{N(N+1)} \quad (5)$$

These formulas provide a good approximation only in the neighbourhood of *Hund's* case *b*.

${}^6\Sigma$ Terms. The formulas of the ${}^6\Sigma$ terms are obtained from (3) by putting $A = 0$:

$$F_i(N) = v_0 + BN(N+1) - DN^2(N+1)^2 + H_i^{ss}(N) + H_i^{sr}(N) \quad (6)$$

where $i = J - 5/2, \dots, J + 5/2$. These formulas were also given by Rao [185].

In the CrH molecule, Kleman and Uhler [93] analysed a ${}^6\Sigma$ - ${}^6\Sigma$ transition and determined by (6) the constants in the formulas for both ${}^6\Sigma$ terms. In doing so, however, they found a discrepancy between experiment and theory, the nature of which has not so far been clarified; nor was it found out whether they can be interpreted by the considerations below.

As regards perturbations by farther-lying terms, the ${}^6\Sigma$ terms behave in a manner similar to the terms of lower multiplicity. The dependence on the rotational quantum number will deviate from (6) if among the perturbing terms a ${}^6\Pi$ term is close to the ${}^6\Sigma$ term. The deviations arising in this case were calculated by Kovács [113]:

$$\begin{aligned} \Delta F_1(N) &= -5[\sigma(N+1) - \tau]N^2 \\ \Delta F_2(N) &= -[\sigma(3N-5)(N+1) + \tau(N+15)]N \\ \Delta F_3(N) &= -[\sigma N(N+1)(N-8) + 2\tau(2N-3)(N+4)] \\ \Delta F_4(N) &= +[\sigma N(N+1)(N+9) - 2\tau(2N+5)(N-3)] \\ \Delta F_5(N) &= +[\sigma(3N+8)N - \tau(N-14)](N+1) \\ \Delta F_6(N) &= +5[\sigma N + \tau](N+1)^2 \end{aligned} \quad (7)$$

where the suffixes 1, ..., 6 are abbreviations for $J - 5/2, \dots, J + 5/2$, and

$$\sigma = 2(B_{II} - B_{\Sigma}) \frac{\xi\eta^* + \xi^*\eta}{v^2}; \quad \tau = \frac{2}{3}(B_{II} - B_{\Sigma}) \frac{|\xi|^2}{v^2} \quad (8)$$

ξ and η having meanings similar to those given earlier.

(b) Λ -Type Doubling. As in the quintet terms, the determination of the intermediate form for the Λ -type doubling is difficult. On the other hand, the case *b* form is relatively simple:

$$\begin{aligned} \Delta v({}^6\Pi_{J-5/2}) &= -\frac{20}{27}\alpha_0 \frac{N}{2N+3} - \alpha_1 N + \alpha_2 N(N+1) \\ \Delta v({}^6\Pi_{J-3/2}) &= -\frac{2}{27}\alpha_0 \left[1 + \frac{27}{2N+3} \right] - \frac{1}{5}\alpha_1(3N-5) + \alpha_2 N(N+1) \\ \Delta v({}^6\Pi_{J-1/2}) &= -\frac{2}{27}\alpha_0 \left[4 + \frac{27}{2N+3} - \frac{15}{2N-1} \right] - \frac{1}{5}\alpha_1(N-8) + \\ &\quad + \alpha_2 N(N+1) \end{aligned} \quad (9)$$

$$\begin{aligned}
 \Delta v(^6\Pi_{J+1/2}) &= -^{2/27}\alpha_0 \left[4 + \frac{15}{2N+3} - \frac{27}{2N-1} \right] + ^{1/5}\alpha_1(N+9) + \\
 &\quad + \alpha_2 N(N+1) \\
 \Delta v(^6\Pi_{J+3/2}) &= -^{2/27}\alpha_0 \left[1 - \frac{27}{2N-1} \right] + ^{1/5}\alpha_1(3N+8) + \alpha_2 N(N+1) \\
 \Delta v(^6\Pi_{J+5/2}) &= +^{20/27}\alpha_0 \frac{N+1}{2N-1} + \alpha_1(N+1) + \alpha_2 N(N+1)
 \end{aligned}$$

where

$$\alpha_0 = \sum (-1)^x \frac{|\xi|^2}{\nu}; \quad \alpha_1 = 2 \sum (-1)^x \frac{\xi \eta^* + \xi^* \eta}{\nu}; \quad \alpha_2 = 8 \sum (-1)^x \frac{|\eta|^2}{\nu} \quad (10)$$

No analysis of A -type doubling in sextet terms has so far been reported.

2.1.8. Septet Terms

(a) General Theory for Spin Splitting. By the procedure used in the foregoing cases, we obtain for septet states in the neighbourhood of case b (Rao [186]):

$$\begin{aligned}
 T_{J-3}(N) &= v_0 + B \left[N(N+1) - A^2 + \frac{3YA^2}{N+1} + \varphi_{J-3}(N) \right] \\
 T_{J-2}(N) &= v_0 + B \left[N(N+1) - A^2 + \frac{YA^2(2N-3)}{N(N+1)} + \varphi_{J-2}(N) \right] \\
 T_{J-1}(N) &= v_0 + B \left[N(N+1) - A^2 + \frac{YA^2(N-5)}{N(N+1)} + \varphi_{J-1}(N) \right] \\
 T_J(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{6YA^2}{N(N+1)} + \varphi_J(N) \right] \\
 T_{J+1}(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{YA^2(N+6)}{N(N+1)} - \varphi_{J+1}(N) \right] \\
 T_{J+2}(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{YA^2(2N+5)}{N(N+1)} - \varphi_{J+2}(N) \right] \\
 T_{J+3}(N) &= v_0 + B \left[N(N+1) - A^2 - \frac{3YA^2}{N} - \varphi_{J+3}(N) \right]
 \end{aligned} \quad (1)$$

where

$$\varphi_{J-3}(N) = 3A^2 Y^2 \frac{(N+2)(N+4)[(N+1)^2 - A^2]}{(N+1)(2N+3)[YA^2(N+7) - 2(N+1)^2(N+2)]}$$

$$\begin{aligned} \varphi_{J-2}(N) &= 5A^2 Y^2 \times \\ &\times \frac{N^2(N+2)(2N+7)[(N+1)^2 - A^2]}{(N+1)(2N+1)(2N+3)[YA^2(N-1)(N+6) - 2N(N+1)^2(N+2)]} \\ &\quad - \varphi_{J-3}(N-1) \end{aligned}$$

$$\begin{aligned} \varphi_{J-1}(N) &= 6A^2 Y^2 \times \\ &\times \frac{N(N+2)(N+3)(2N-1)[(N+1)^2 - A^2] -}{(N+1)(2N+1)(2N+3)[YA^2(N-2)(N+5) - 2N(N+1)^2(N+2)]} \\ &\quad - \varphi_{J-2}(N-1) - \varphi_{J-3}(N-2) \end{aligned}$$

$$\begin{aligned} \varphi_J(N) &= [\varphi_{J+3}(N+3) + \varphi_{J+2}(N+2) + \varphi_{J+1}(N+1)] - \\ &\quad - [\varphi_{J-1}(N-1) + \varphi_{J-2}(N-2) + \varphi_{J-3}(N-3)] \quad (2) \end{aligned}$$

$$\begin{aligned} \varphi_{J+1}(N) &= 6A^2 Y^2 \times \\ &\times \frac{(N-2)(N-1)(N+1)(2N+3)[N^2 - A^2]}{N(2N-1)(2N+1)[YA^2(N-4)(N+3) - 2(N-1)N^2(N+1)]} \\ &\quad - \varphi_{J+2}(N+1) - \varphi_{J+3}(N+2) \end{aligned}$$

$$\begin{aligned} \varphi_{J+2}(N) &= 5A^2 Y^2 \times \\ &\times \frac{(N-1)(N+1)^2(2N-5)[N^2 - A^2]}{N(2N-1)(2N+1)[YA^2(N-5)(N+2) - 2(N-1)N^2(N+1)]} \\ &\quad - \varphi_{J+3}(N+1) \end{aligned}$$

$$\varphi_{J+3}(N) = 3A^2 Y^2 \frac{(N-3)(N-1)[N^2 - A^2]}{N(2N-1)[YA^2(N-6) - 2(N-1)N^2]}$$

The full term formulas complemented with the usual correction terms are

$$F_i(N) = T_i(N) + H_i^c(N) + H_i^{ss}(N) + H_i^{sr}(N) \quad (3)$$

where $i = J-3, J-2, J-1, J, J+1, J+2, J+3$; the expression of $H_i^c(N)$ is to be taken from (2.1.1-6); and by (2.1.1-7a, b), (2.1.1-8) $H_i^{ss}(N) + H_i^{sr}(N)$ are of the form

$$H_{J-3}^{ss}(N) + H_{J-3}^{sr}(N) = -15\epsilon \frac{N}{2N+3} \Phi^+(N) + 3\gamma N \sigma(N)$$

$$\begin{aligned}
H_{J-2}^{ss}(N) + H_{J-2}^{sr}(N) &= + \frac{45\varepsilon}{2N+3} \Phi^+(N) + \gamma(2N-3)\sigma(N) \\
H_{J-1}^{ss}(N) + H_{J-1}^{sr}(N) &= + \frac{9}{2}\varepsilon \left[1 + \frac{12}{2N+3} - \frac{5}{2N-1} \right] \Phi^+(N) + \\
&\quad + \gamma(N-5)\sigma(N) \\
H_J^{ss}(N) + H_J^{sr}(N) &= + 3\varepsilon \left[2 + \frac{15}{2N+3} - \frac{15}{2N-1} \right] \Phi^+(N) - 6\gamma\sigma(N) \\
H_{J+1}^{ss}(N) + H_{J+1}^{sr}(N) &= + \frac{9}{2}\varepsilon \left[1 - \frac{12}{2N-1} + \frac{5}{2N+3} \right] \Phi^+(N) - \\
&\quad - \gamma(N+6)\sigma(N) \\
H_{J+2}^{ss}(N) + H_{J+2}^{sr}(N) &= - \frac{45\varepsilon}{2N-1} \Phi^+(N) - \gamma(2N+5)\sigma(N) \quad (4) \\
H_{J+3}^{ss}(N) + H_{J+3}^{sr}(N) &= - 15\varepsilon \frac{N+1}{2N-1} \Phi^+(N) - 3\gamma(N+1)\sigma(N)
\end{aligned}$$

where $\Phi^+(N)$ and $\sigma(N)$ are the same as in (2.1.6-5).

${}^7\Sigma$ Terms. For the ${}^7\Sigma$ terms we obtain, by putting $A = 0$,

$$F_i(N) = v_0 + BN(N+1) - DN^2(N+1)^2 + H_i^{ss}(N) + H_i^{sr}(N) \quad (5)$$

where $i = J-3, \dots, J+3$. These formulas were given by Nevin [166] who also applied them to the ${}^7H-{}^7\Sigma$ transition of the MnH molecule (see also Nevin [165] and Nevin and Doyle [169]). Nevin found that (5) does not accurately describe the change of the observed ${}^7\Sigma$ term vs. the rotational quantum number, but that it appears as if the constant γ would 'change' as a function of the rotational quantum number. All these observations imply that some correction is necessary for the accurate description of the phenomena. This problem will be dealt with below.

Perturbation by farther-lying terms does not change the dependence on the rotational quantum number in the case of the ${}^7\Sigma$ states, either; only the constants are changed. If, however, a 7H term lies sufficiently close, there is a deviation from formula (5); according to Kovács [102, 113],

$$\begin{aligned}
\Delta F_1(N) &= - [3\sigma(N+1)(N+2) - \tau(9N+4)]N \\
\Delta F_2(N) &= - [\sigma(N+1)(2N+3) - \tau(4N-11)]N \\
\Delta F_3(N) &= - [\sigma N(N+1)^2 - \frac{1}{2}\tau(N-5)(2N-9)] \\
\Delta F_4(N) &= 0 \\
\Delta F_5(N) &= + [\sigma N^2(N+1) + \frac{1}{2}\tau(N+6)(2N+11)] \\
\Delta F_6(N) &= + [\sigma N(2N-1) + \tau(4N+15)](N+1) \\
\Delta F_7(N) &= + [3\sigma(N-1)N + \tau(9N+5)](N+1)
\end{aligned} \quad (6)$$

where the suffixes $i = 1, \dots, 7$ are a shorthand notation for $J - 3, \dots, J + 3$ and the quantities σ and τ are the same as in (2.1.6-8). By Formula (6), the deviations observed by Nevin can be satisfactorily interpreted. It can be concluded therefore that the apparent dependence of γ on the rotational quantum number is cancelled when expression (5) is complemented with (6). The observed and calculated deviations are compared in Fig. 2.17. The calculated values are due to Kovács [103, 119] who derived them from Formula (6).

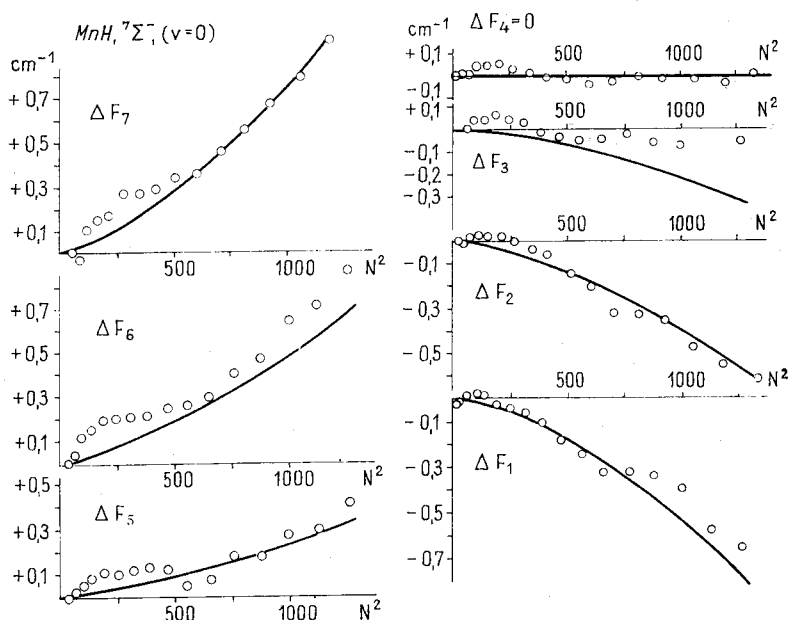


Fig. 2.17 Deviations from the spin splittings calculated by means of formula (5) for the ${}^7\Sigma^-$ term of the MnH molecule, according to Kovács [103, 111, 113]. In Equation (6) of the theoretical curves, $\sigma = 6.56 \times 10^{-6} \text{ cm}^{-1}$, $\tau = 1.44 \times 10^{-6} \text{ cm}^{-1}$.

${}^7\Pi$ Terms. The higher state of the septet transition observed in the MnH molecule is a ${}^7\Pi$ term. Further ${}^7\Pi$ - ${}^7\Sigma$ transitions were observed by Nevin and co-workers [167, 168] in the MnD molecule, by Hayes and Nevin [67] in the MnCl and MnBr molecules. As yet no author has attempted to apply Formula (3).

(b) Λ -Type Doubling. The Λ -type splittings of the ${}^7\Pi$ terms are in case b

$$\Delta\nu({}^7\Pi_{J-3}) = +\frac{5}{6}\alpha_0 \frac{N}{2N+3} - \alpha_1 N + \alpha_2 N(N+1)$$

$$\Delta\nu({}^7\Pi_{J-2}) = -\frac{15}{6}\alpha_0 \frac{1}{2N+3} - \frac{1}{3}\alpha_1(2N-3) + \alpha_2 N(N+1)$$

$$\Delta\nu({}^7\Pi_{J-1}) = -\frac{1}{4}\alpha_0 \left[1 + \frac{12}{2N+3} - \frac{5}{2N-1} \right] - \frac{1}{3}\alpha_1(N-5) + \alpha_2 N(N+1)$$

$$\Delta v(^7\Pi_J) = -\frac{1}{6}\alpha_0 \left[2 + \frac{15}{2N+3} - \frac{15}{2N-1} \right] + 2\alpha_1 + \alpha_2 N(N+1) \quad (7)$$

$$\Delta v(^7\Pi_{J+1}) = -\frac{1}{4}\alpha_0 \left[1 - \frac{12}{2N-1} + \frac{5}{2N+3} \right] + \frac{1}{3}\alpha_1(N+6) + \alpha_2 N(N+1)$$

$$\Delta v(^7\Pi_{J+2}) = +\frac{15}{6}\alpha_0 \frac{1}{2N-1} + \frac{1}{3}\alpha_1(2N+5) + \alpha_2 N(N+1)$$

$$\Delta v(^7\Pi_{J+3}) = +\frac{5}{6}\alpha_0 \frac{N+1}{2N-1} + \alpha_1(N+1) + \alpha_2 N(N+1)$$

where

$$\alpha_0 = \sum (-1)^x \frac{|\xi|^2}{\nu} + 18\alpha; \quad \alpha_1 = 2 \sum (-1)^x \frac{\xi \eta^* + \xi^* \eta}{\nu}; \quad \alpha_2 = 8 \sum (-1)^x \frac{|\eta|^2}{\nu} \quad (8)$$

and the constants have meanings similar to those given previously.

Nevin and his co-workers described in the above papers cases of A -type doubling in the septet transitions of the MnH and MnD molecules. Since case b does not seem to be a good approximation for these $^7\Pi$ terms, it is doubtful whether the observed deviations can be interpreted by (7).

2.2. L -MULTIPLETS

As has been seen above, parallel to the de-coupling of the resultant spin momentum of the electrons from the inter-nuclear axis, as rotation increases (i.e. as the transition between *Hund's* cases a and b proceeds) the orbital angular momentum \vec{L} also starts to de-couple. It is this phenomenon, regarded as the beginning of the transition towards *Hund's* case d , that gives rise to A -type doubling. So far the splitting caused by the initial de-coupling of the orbital angular momentum, i.e. A -type doubling compared with the spin multiplet splitting has been negligible in a first approximation. As, however, L de-coupling proceeds, the splitting caused by it also becomes greater and can become so strong that it is the spin multiplet splitting that can be neglected in a first approximation. In the case of total de-coupling, i.e. in *Hund's* case d , the interaction between the vector of the orbital angular momentum and the inter-nuclear axis disappears; instead, the vector in question is coupled to the quantized angular momentum vector of nuclear rotation ($\vec{R} = \hbar \sqrt{R(R+1)}$) and leads to the like-

wise quantized resultant vector N (Fig. 1.7) whose quantum number can assume

$$N = (R + L), (R + L - 1), \dots, (R - L) \quad (1)$$

It is especially in the case of light molecules that the gradual L de-coupling, i.e. the transition between *Hund's* cases b and d can frequently be observed. In the following, these transitional cases will be dealt with the spin being neglected in a first approximation. Here again, one of two procedures may be applied: one may start either from *Hund's* case b or from *Hund's* case d . Both approaches have been tried. We shall start from case b in the following discussion.

The intermediate-case energy expressions will be derived first by considering the energy expressions of case b as an unperturbed system; then the interaction between the orbital angular momentum \vec{L} and the inter-nuclear axis will be accounted for, and so will, by (1.5-10), the terms neglected on the separation of the wave equation. In the possession of these energy expressions we shall then proceed to determine the elements of the transformation matrix by (1.5-9); subsequently, we shall derive the intermediate form of the centrifugal term from (1.5-15).

In addition to the above, in one special case the spin will also be taken into account together with the L -multiplet.

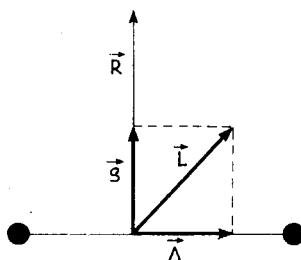


Fig. 2.18 Relation between the resultant orbital angular momentum of a molecule and the molecular axis in *Hund's* cases b and d .

2.2.1.1. Energies and Perturbation-Matrix Elements in the Limiting Cases

In order to carry out the calculations proposed above, the limiting case energy expressions and the perturbation-matrix elements are required. The total neglect of spin entails the disappearance of all interactions connected with it: they are replaced by the interaction of the vector L with the inter-nuclear axis, which in a first approximation has according to Hill and van Vleck [77] the form

$$H^0 = C(\vec{L} \cos \alpha)^2 \quad (1)$$

where α is the angle between the vector \vec{L} and the inter-nuclear axis. In *Hund's* case b , $\vec{L} \cos \alpha = \Lambda$ (Fig. 2.18) and the interaction will be

$$H_b^0 = C\Lambda^2 \quad (2)$$

In case d —let q denote the quantized component parallel to \vec{R} of vector \vec{L} —we obtain instead of (2)

$$H_d^0 = \frac{1}{2}C[L(L+1) - q^2] \quad (3)$$

By these considerations and some previous ones, the case *b* term values and the perturbation-matrix elements are the following:

$$T_A(N) = v_0 + CA^2 + B[N(N+1) - A^2 + L(L+1) - A^2] \quad (4a)$$

$$H_b^a(A, N; A \pm 1, N) = B[L(L+1) - A(A \pm 1)]^{1/2} [N(N+1) - A(A \pm 1)]^{1/2} \quad (4b)$$

$$H_b^c(A, N; A, N) = -D\{[N(N+1) - L(L+1) - 2A^2]^2 + 2[N(N+1) - A^2][L(L+1) - A^2] + 2A^2\} \quad (5a)$$

$$H_b^c(A, N; A \pm 1, N) = -2D[N(N+1) + L(L+1) - 2A(A \pm 1) - 1] \times \\ \times [L(L+1) - A(A \pm 1)]^{1/2} [N(N+1) - A(A \pm 1)]^{1/2} \quad (5b)$$

$$H_b^c(A, N; A \pm 2, N) = -D[L(L+1) - A(A \pm 1)]^{1/2} [L(L+1) - (A \pm 1)(A \pm 2)]^{1/2} [N(N+1) - A(A \pm 1)]^{1/2} \times \\ \times [N(N+1) - (A \pm 1)(A \pm 2)]^{1/2} \quad (5c)$$

where Formula (4a) is derived from (2), (1.1-41) and (1.3-30); (4b) from (1.3-24); and (5a, b, c) from (1.4-15a, b, c).

In case *d* the term values become

$$T_d(R) = v_0 + \frac{1}{2}C[L(L+1) - \varrho^2] + BR(R+1) \\ H_d^c(R) = -DR^2(R+1)^2; \quad R = N - \varrho \quad (6)$$

For *Hund's* cases *b* and *d* we can regard $\alpha = C/B$, the ratio of the coupling constant *C*, as characteristic of the coupling between the vector \vec{L} and the internuclear axis, to the rotational constant *B*. In case *b*, $\alpha \gg N(N+1)$; in case *d*, $\alpha \ll R(R+1)$. Just as in the case of the spin multiplets, term formulas valid for any value of *S* (the spin value) could be given for the limiting cases, we can also in the present case give term formulas valid for any value of *L* in the limiting cases (i.e. in cases *b* and *d*).

$$F_b(L, \alpha \gg N(N+1)) = v_0 + CA^2 + B[N(N+1) - A^2 + L(L+1) - A^2] + H_b^c(A, N; A, N) \quad (7)$$

and

$$F_d(L, \alpha \ll R(R+1)) = v_0 + \frac{1}{2}C[L(L+1) - \varrho^2] + BR(R+1) - DR^2(R+1)^2 \quad (8)$$

The above limiting-case formulas, however, rarely agree with experience. For the intermediate cases, formulas which are not general from the point of view of L , i.e. which hold only for a *given* L but for *any* value of α , i.e. $F(L = \text{const.}, \alpha)$ are preferable. Such formulas can be obtained by starting from case b , with the perturbation-matrix elements given in (4b) and (5b, c) taken for a given value of L , according to the methods of perturbation calculation. The different values of L lead to different cases. Of these, only two will be dealt with here, namely when $L = 1$, (the case of the *p-term complex*) and when $L = 2$ (the case of *d-term complex*).

2.2.2. *p-Term Complex*

When $L = 1$, then by (2.2.1-4a, b) and (1.5-10), a first-degree and a second-degree secular equation result:

$$\begin{aligned} \Pi_a: T &= T_1^0 \\ \Sigma_b: \begin{vmatrix} T_0^0 - T & H_{01}^p \\ H_{10}^p & T_1^0 - T \end{vmatrix} &= 0 \end{aligned} \quad (1a)$$

their elements are

$$\begin{aligned} T_0^0 &= v_0 + B[N(N+1) + 2]; \quad H_{01}^p = 2B\sqrt{N(N+1)} \\ T_1^0 &= v_0 + C + BN(N+1) \end{aligned} \quad (1b)$$

The solution is given by the expressions

$$\begin{aligned} \Sigma_b: T_{N+1}(N) &= v_0 + B \left[\frac{\alpha}{2} + N(N+1) + 1 - \sqrt{\frac{\alpha}{4}(\alpha-4) + (2N+1)^2} \right] \\ \Pi_a: T_N(N) &= v_0 + B[\alpha + N(N+1)] \\ \Pi_b: T_{N+1}(N) &= v_0 + B \left[\frac{\alpha}{2} + N(N+1) + 1 + \sqrt{\frac{\alpha}{4}(\alpha-4) + 2N+1)^2} \right] \end{aligned} \quad (2)$$

where $\alpha = C/B$ and the values $N-1$, N , $N+1$ in the suffix denote the possible values of the case d quantum number R ; the case b term from which the term in question originates is marked on the left. These formulas were first given by Hill and van Vleck [77] who chose case d as the unperturbed system. It is apparent that for $\alpha = 0$, i.e. for case d , (2) reduces to $BR(R+1)$, where R can be $N-1$, N or $N+1$, whereas in the case $\alpha \gg N(N+1)$ a power series development yields

$$\Sigma_b: T_{N-1}(N) = v_0 + B[N(N+1) + 2] - 4 \frac{B^2}{C} N(N+1) \quad (3a)$$

$$\Pi_a: T_N(N) = v_0 + C + BN(N+1) \quad (3b)$$

$$\Pi_b: T_{N+1}(N) = v_0 + C + BN(N+1) + 4 \frac{B^2}{C} N(N+1) \quad (3c)$$

where the last terms in (3a) and (3c) are identical with the last terms of (2.1.2-2) and (2.1.2-9), taken for a single Σ term under the assumption of 'pure precession'. Thus the expression obtained for the difference $T_N(N) - T_{N+1}(N)$ is the same as the one derived for Λ -type doubling in (2.1.2-10).

Using (2), the elements of the transformation matrix can also be calculated by (1.5-9). Then,

$$\begin{aligned} S_{0N,-1} &= \sqrt{\frac{2N(N+1)}{C^-(N)}}; & S_{1,N-1} &= -\frac{u^-(N)}{\sqrt{2C^-(N)}} \\ S_{0,N+1} &= \sqrt{\frac{2N(N+1)}{C^+(N)}}; & S_{1,N+1} &= \frac{u^+(N)}{\sqrt{2C^+(N)}} \end{aligned} \quad (4)$$

where

$$\begin{aligned} u^\pm(N) &= \left[\frac{\alpha}{4}(\alpha - 4) + (2N + 1)^2 \right]^{1/2} \pm \frac{1}{2}(\alpha - 2) \\ C^\pm(N) &= \frac{1}{2}[u^\pm(N)^2 + 4N(N + 1)] \end{aligned} \quad (5)$$

In more rigorous investigations, however, the term Formula (2) has to be complemented with the centrifugal correction. In the intermediate cases between cases *b* and *d* the intermediate form of the centrifugal correction term is required. To find it let us start from (2.2.1-5a, b, c). The general formulas yield for this case

$$\begin{aligned} H_b^c(0, 0) &= -D[N^2(N + 1)^2 + 8N(N + 1) + 4] \\ H_b^c(+1, -1) &= -2DN(N + 1) \\ H_b^c(1, 1) &= -D[N^2(N + 1)^2 + 2N(N + 1)] \\ H_b^c(0, 1) &= -2D[N(N + 1) + 1]\sqrt{2N(N + 1)} \end{aligned} \quad (6)$$

For the intermediate case between cases *b* and *d* we obtain by (6), (4) and (1.5-15)

$$\begin{aligned} H_R^c(N) &= -D\{N^2(N + 1)^2 + 4N(N + 1) - 4S_{0,R}[N(N + 1) + 1] \times \\ &\times [S_{0,R} + 2S_{1,R}\sqrt{N(N + 1)}]\} \end{aligned} \quad (7)$$

where $R = N - 1, N + 1$. It should be noted that the Π eigenfunctions are of the form $\psi(\Pi_1) = 1/\sqrt{2}[\psi(\Pi_{+1}) \pm \psi(\Pi_{-1})]$, resulting in a factor of $\sqrt{2}$ in $H_b^c(0, 1)$. Formula (7) yields the diagonal elements of (6) if $\alpha \gg N$, i.e. a transition takes place towards case *b*, whereas for $\alpha = 0$, (7) assumes the case *d* form

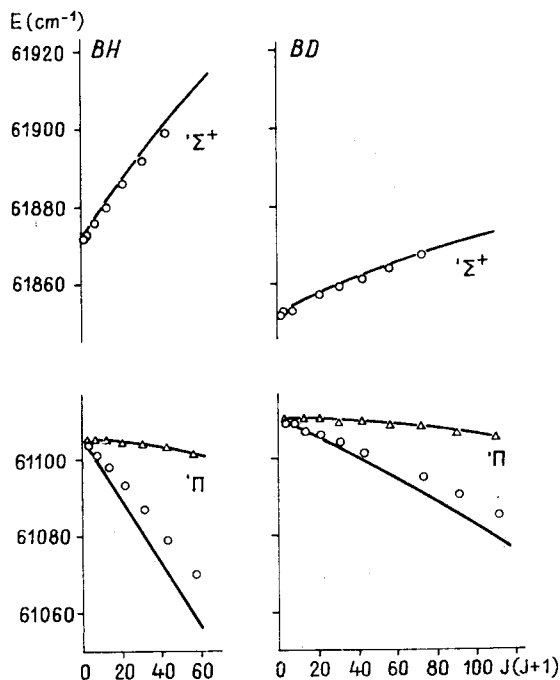
$$H_d^c(R) = -DR^2(R + 1)^2 \quad (8)$$

By the foregoing considerations the full term formulas of the p -term complex will in the intermediate case between *Hund's* cases b and d be

$$F_R(N) = T_R(N) + H_R^c(N) \quad (9)$$

where $R = N - 1, N, N + 1$.

An experimental application of (2) can be found in Bauer, Herzberg and Johns [12] who applied Formula (9) to the $3p$ -term complex of the molecules



Figs 2.19 and 2.20 Difference between (9) and $BN(N+1)$ for the $3p$ -term complex of the BH and BD molecules, according to Bauer, Herzberg and Johns [12]. The constants in Formula (9) are, for BH: $B = 12.321 \text{ cm}^{-1}$, $D = 1.3 \times 10^{-3} \text{ cm}^{-1}$, $\alpha = -60.25 \text{ cm}^{-1}$; for BD: $B = 6.736 \text{ cm}^{-1}$, $D = 0.4 \times 10^{-3} \text{ cm}^{-1}$, $\alpha = -108.24 \text{ cm}^{-1}$.

BH and BD in the neighbourhood of 1625 \AA and found between Formula (9) and $BN(N+1)$ the differences shown in Figs 2.19 and 2.20. The above authors interpreted the slight deviations as a result of the influence of a different electronic state.

2.2.3. *d*-Term Complex

When $L = 2$ (i.e. in the *d*-term complex case), we obtain a second-order secular equation and a third-order one by (1.5-10) and (2.2.1-4a, b). These secular equations are

$$\begin{array}{l} \Pi_b : \left| \begin{array}{ccc} T_1^0 - T & H_{12} & \\ H_{21} & T_2^0 - T & \end{array} \right| = 0 \\ A_b : \left| \begin{array}{ccc} T_1^0 - T & H_{01} & 0 \\ H_{10} & T_1^0 - T & H_{12} \\ 0 & H_{21} & T_1^0 - T \end{array} \right| = 0 \end{array} \quad (1)$$

where

$$\begin{aligned} T_0^0 &= v_0 + B[N(N+1) + 6] & ; & & H_{01} &= 2B\sqrt{3N(N+1)} \\ T_1^0 &= v_0 + C + B[N(N+1) + 4] & ; & & H_{12} &= 2B\sqrt{(N-1)(N+2)} \\ T_2^0 &= v_0 + 4C + B[N(N+1) - 2] & ; & & & \end{aligned} \quad (2)$$

The solution of equation (1) is, by (1.5-26) and (2.1.4-3),

$$\begin{aligned} \Sigma_a : T_{N-2}(N) &= v_0 + B[1/3(5\alpha + 8) + N(N+1) - 2u_2(N) - \\ &\quad - 1/2(\alpha - 2)(v(N) - 2/3)] \\ \Pi_b : T_{N-1}(N) &= v_0 + B[5/2\alpha + 1 + N(N+1) - u_1(N)] \\ \Pi_a : T_N(N) &= v_0 + B[1/3(5\alpha + 8) + N(N+1) + (\alpha - 2)(v(N) - 2/3)] \\ A_b : T_{N+1}(N) &= v_0 + B[5/2\alpha + 1 + N(N+1) + u_1(N)] \\ A_a : T_{N+2}(N) &= v_0 + B[1/3(5\alpha + 8) + N(N+1) + 2u_2(N) - \\ &\quad - 1/2(\alpha - 2)(v(N) - 2/3)] \end{aligned} \quad (3)$$

where

$$\begin{aligned} u_1(N) &= \sqrt{9/4\alpha(\alpha - 4) + (2N + 1)^2} \\ u_2(N) &= \sqrt{13/12\alpha(\alpha - 4) + 4/3 + (2N + 1)^2} \\ v(N) &= 2/3 \left(1 + \frac{2(2N + 1)^2 - 35/36\alpha(\alpha - 4) - 8/9}{u_2(N)^2} \right) \end{aligned} \quad (4)$$

These formulas were first given by Kovács and Budó [123]. Putting $\alpha = 0$, (3) reduces to $BR(R+1)$, where $R = N-2, N-1, N, N+1, N+2$, whereas $\alpha \gg N(N+1)$ yields the case *b* form in a first approximation:

$$CA^2 + B[N(N+1) + 6 - 2A^2]$$

Starting from case *d* Dieke [41] gave a derivation of Formula (3) by a power-series development in the neighbourhoods of cases *b* and *d*.

By (3) and (1.5-9) the transformation-matrix elements become

$$\begin{aligned} S_{1,N-1} &= \sqrt{\frac{2(N-1)(N+2)}{C^-(N)}}; & S_{2,N-1} &= -\frac{u^-(N)}{\sqrt{2C^-(N)}} \\ S_{1,N+1} &= \sqrt{\frac{2(N-1)(N+2)}{C^+(N)}}; & S_{2,N+1} &= \frac{u^+(N)}{\sqrt{2C^+(N)}} \end{aligned} \quad (5a)$$

$$\begin{aligned} S_{0,N-2} &= -\sqrt{\frac{3N(N+1)}{C_\Sigma(N)}} u_\Sigma^+(N); & S_{1,N-2} &= \frac{u_\Sigma^+(N) u_\Sigma^-(N)}{\sqrt{C_\Sigma(N)}} \\ S_{2,N-2} &= -\sqrt{\frac{(N-1)(N+2)}{C_\Sigma(N)}} u_\Sigma^-(N) \\ S_{0,N} &= -\sqrt{\frac{12N(N+1)}{C_{II}(N)}} (3-v(N)); & S_{1,N} &= -\frac{(3-v(N))(1+v(N))}{\sqrt{C_{II}(N)}} \\ S_{2,N} &= \sqrt{\frac{4(N-1)(N+2)}{C_{II}(N)}} (1+v(N)) \end{aligned} \quad (5b)$$

$$\begin{aligned} S_{0,N+2} &= \sqrt{\frac{3N(N+1)}{C_A(N)}} u_A^-(N); & S_{1,N+2} &= \frac{u_A^-(N) u_A^+(N)}{\sqrt{C_A(N)}} \\ S_{2,N+2} &= \sqrt{\frac{(N-1)(N+2)}{C_A(N)}} u_A^+(N) \end{aligned}$$

where

$$u^\pm(N) = u_1(N) \pm \frac{3}{2}(\alpha - 2); \quad C^\pm(N) = \frac{1}{2}[u^\pm(N)^2 + 4(N-1)(N+2)]$$

$$\begin{aligned} u_\Sigma^\pm(N) &= u_2(N) \pm (\alpha - 2) \left(1 \pm \frac{v(N)}{4} \right) \\ u_A^\pm(N) &= u_2(N) \pm (\alpha - 2) \left(1 \mp \frac{v(N)}{4} \right) \end{aligned} \quad (6a)$$

$$\begin{aligned} C_\Sigma(N) &= [u_\Sigma^-(N)^2 + 3N(N+1)] u_\Sigma^+(N)^2 + (N-1)(N+2) u_\Sigma^-(N)^2 \\ C_{II}(N) &= [(\alpha - 2)(1+v(N))^2 + 12N(N+1)] (3-v(N))^2 + \\ &\quad + 4(N-1)(N+2)(1+v(N))^2 \end{aligned} \quad (6b)$$

$$C_A(N)^2 = [u_A^+(N)^2 + 3N(N+1)] u_A^-(N)^2 + (N-1)(N+2) u_A^+(N)^2$$

As in the previous cases, Formula (3) is to be complemented with the centrifugal correction, more precisely with its intermediate form between cases

b and d . For the elements of the matrix of case b , by (2.2.1-5a,b,c), we have

$$\begin{aligned}
 H_b^e(0, 0) &= -D[N^2(N+1)^2 + 24N(N+1) + 36] \\
 H_b^e(1, 1) &= -D[N^2(N+1)^2 + 18N(N+1) + 8] \\
 H_b^e(2, 2) &= -D[N^2(N+1)^2 - 4] \\
 H_b^e(0, 1) &= -2D[N(N+1) - 5] \sqrt{6N(N+1)} \\
 H_b^e(1, 2) &= -4D[N(N+1) + 1] \sqrt{N(N+1) - 2} \\
 H_b^e(0, 2) &= -2D \sqrt{6N(N+1)[N(N+1) - 2]} \\
 H_b^e(+1, -1) &= -6DN(N+1)
 \end{aligned} \tag{7}$$

By the above formulas and (5a), (5b) we obtain for the intermediate case between b and \tilde{a} :

$$\begin{aligned}
 H_R^e(N) &= S_{0,R}^2 H_b^e(0, 0) + S_{1,R}^2 (H_b^e(1, 1) + H_b^e(+1, -1)) + S_{2,R}^2 H_b^e(2, 2) + \\
 &+ 2S_{0,R} S_{1,R} H_b^e(0, 1) + 2S_{1,R} S_{2,R} H_b^e(1, 2) + 2S_{0,R} S_{2,R} H_b^e(0, 2)
 \end{aligned} \tag{8}$$

where $R = N - 2, N, N + 2$, or, if the terms with zero suffix are neglected, $R = N - 1, N + 1$. If $\alpha \gg N(N + 1)$, Formula (8) reduces to case b , yielding the diagonal terms of (7), whereas if $\alpha = 0$, it assumes the form of (2.2.2-8).

Accordingly, the complete term formulas for the case of the d -term complex will be

$$F_R(N) = T_R(N) + H_R^e(N) \tag{9}$$

where $R = N - 2, N - 1, N, N + 1, N + 2$.

Formula (3) was applied by Kovács and Budó [123] to the $4d$ -term complex of the He_2 molecule, which, although a triplet transition, exhibits a splitting so weak as to be negligible. The result is shown in Fig. 2.21.

The generally made assumption that the coupling between the orbital angular momentum and the inter-nuclear axis can be described by the expression CA^2 (see 2.2.1-1) corresponds to experimental facts only when the excited electron orbit does not penetrate the molecular core. This case is most usual in light molecules (H_2 , He_2). In other cases, e.g. in the NO molecule (Huber and Miescher [81]) and in the $3d$ -term complex of the BH and BD molecules (Bauer, Herzberg and Johns [12]) there are deviations from the above expression. Chiu [35] has pointed out that the form CA^2 is the first term of an infinite multipole expansion, and that further approximations lead to the result that in the case of d -term complexes a bi-parametric development is necessary, where the two parameters are

the energy differences $\nu(A; II)$ and $\nu(II; \Sigma)$. Chiu [35] succeeded in generalizing formula (3) taking these parameters into consideration. A more detailed discussion can be found in Ginter [66a,b,c].

It is to be noted that Formula (3) can be produced also by starting from case *d*. The perturbation-matrix elements necessary to do so were given by Hill and van Vleck [77].

In terms of higher multiplicity, when the spin-multiplet splitting cannot be neglected, a complicated case results as it is difficult to treat mathematically the many interacting states. If, however, in the case of a *d*-term complex a term (e.g. a Δ -term) lies so far that no interactions involving it have to be taken into account the doublet case is readily treated.

A case in point is the *d*-term complex formed by the $H^2\Sigma^+$ and $H'^2\Pi$ terms of the NO molecule.

If the interactions mentioned above are neglected, it is sufficient to take into account the interactions between the following six components: $^2\Sigma_1^+$, $^2\Pi_{c1}$, $^2\Pi_{d1}(N=J-1/2)$, $^2\Sigma_2^+$, $^2\Pi_{c2}$, $^2\Pi_{d2}(N=J+1/2)$. The sixth-order secular determinant resulting from (1.5-10) decomposes, however, by symmetry into two third-order determinants as follows:

$$\begin{aligned}
 & \begin{vmatrix} ^2\Pi_{d1}: & T_1^0 - T & H_{12} & H_{13} \\ ^2\Pi_{c2}: & H_{21} & T_2^0 - T & H_{23} \\ ^2\Sigma_2^+: & H_{31} & H_{32} & T_3^0 - T \end{vmatrix} = 0 \\
 & \begin{vmatrix} ^2\Pi_{d2}: & T_4^0 - T & H_{45} & H_{46} \\ ^2\Pi_{c1}: & H_{54} & T_5^0 - T & H_{56} \\ ^2\Sigma_1^+: & H_{64} & H_{65} & T_6^0 - T \end{vmatrix} = 0
 \end{aligned} \tag{10}$$

By (2.1.1-5a, b) and (2.2.1-4a, b) and the case *b* forms of the spin-orbit interaction-matrix elements for $S = 1/2$ (as in Formulas (1.2-36) for $S = 1$;

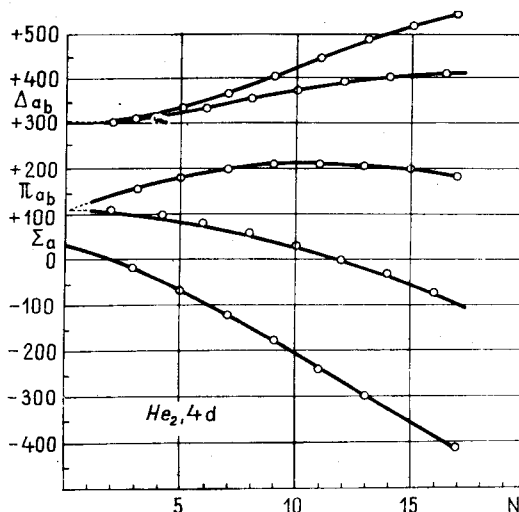


Fig. 2.21 Difference between (9) and $BN(N+1)$ for the $4d$ -term complex of the He_2 molecule, according to Kovács and Budó [123]. The constants in expression (9) are the following: $B_b = 7.084 \text{ cm}^{-1}$, $D_b = -5.28 \times 10^{-4} \text{ cm}^{-1}$, $\alpha_b = 11.28 \text{ cm}^{-1}$, $B_a = 7.063 \text{ cm}^{-1}$, $D_a = -5.01 \text{ cm}^{-1}$, $\alpha_a = 11.32 \text{ cm}^{-1}$. The constants calculated from the two groups of different symmetry are slightly different, probably because the conditions of 'pure precession' are not strictly satisfied.

cf. Kovács [102]) the elements of the above determinants will be the following:

$$T_1^0 = C + B[N(N+1) + 4] + \frac{A}{2(N+1)}; \quad H_{12} = A \frac{\sqrt{N(N+2)}}{2(N+1)}$$

$$T_2^0 = C + B[(N+1)(N+2) + 4] - \frac{A}{2(N+1)} \quad (11a)$$

$$H_{13} = \frac{A}{2} \sqrt{\frac{3N}{N+1}}$$

$$T_3^0 = B[(N+1)(N+2) + 6]; \quad H_{23} = \sqrt{\frac{3(N+2)}{N+1}} \left[\frac{A}{2} + 2B(N+1) \right]$$

$$T_4^0 = C + B[N(N+1) + 4] - \frac{A}{2N}; \quad H_{45} = A \frac{\sqrt{(N-1)(N+1)}}{2N}$$

$$T_5^0 = C + B[(N-1)N + 4] + \frac{A}{2N}; \quad H_{46} = \frac{A}{2} \sqrt{\frac{3(N+1)}{N}} \quad (11b)$$

$$T_6^0 = B[(N-1)N + 6]; \quad H_{56} = \sqrt{\frac{3(N-1)}{N}} \left[\frac{A}{2} - 2BN \right]$$

If those interactions for which $AN = \pm 1$ are neglected in a first approximation, i.e.

$$H_{12} = H_{45} = H_{13} = H_{46} \approx 0$$

both determinants in (10) are easy to solve. Rewriting the solutions so as to make them contain the same value of the rotation quantum number N , we obtain

$${}^2H_{d1}: T_{J-1/2}(N) = B \left[\alpha + 4 + N(N+1) + \frac{Y}{2(N+1)} \right]$$

$$\left. \begin{array}{l} {}^2H_{c2}: T_{J+1/2}(N) \\ {}^2\Sigma_2: T_{J+1/2}(N) \end{array} \right\} = B \left[\frac{1}{2}(\alpha + 10) - \frac{Y}{4N} + N(N+1) \pm \right.$$

$$\left. \pm \frac{1}{2} \sqrt{\left(\alpha - 2 - \frac{Y}{2N} \right)^2 + 3(Y + 4\sqrt{N(N+1)})^2} \right] \quad (12a)$$

$${}^2\Pi_{d2}; T_{J+1/2}(N) = B \left[\alpha + 4 + N(N+1) - \frac{Y}{2N} \right]$$

$$\left. \begin{array}{l} {}^2\Pi_{c1}; T_{J-1/2}(N) \\ {}^2\Sigma_1 : T_{J-1/2}(N) \end{array} \right\} = B \left[\frac{1}{2}(\alpha + 10) + \frac{Y}{4(N+1)} + N(N+1) \pm \right.$$

$$\left. \pm \frac{1}{2} \sqrt{\left(\alpha - 2 + \frac{Y}{2(N+1)} \right)^2 + 3(Y - 4\sqrt{N(N+1)})^2} \right] \quad (12b)$$

$$\left(\alpha = \frac{C}{B}; Y = \frac{A}{B} \right)$$

As shown in Fig. 2.22, in this case the A -type doubling is very strong relatively, i.e. the corresponding levels are rather far apart; at the same time, however, due to the weak spin splitting, the components of the spin doublet are close together. This is the exact reverse of the usual case. For the spin doublet differences, we obtain from (12a) and (12b):

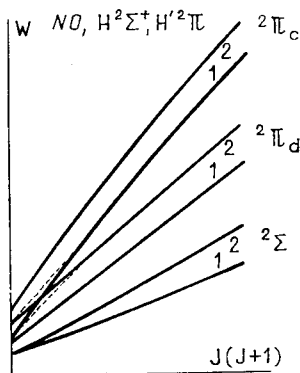


Fig. 2.22 Components of the d -term complex formed by the terms $H^2\Sigma^+$ and $H'^2\Pi$ of the NO molecule vs. the rotational quantum numbers. The components deriving from spin splitting are seen to be situated in the case of ${}^2\Pi$ terms much closer to one another than those deriving from A -type splitting.

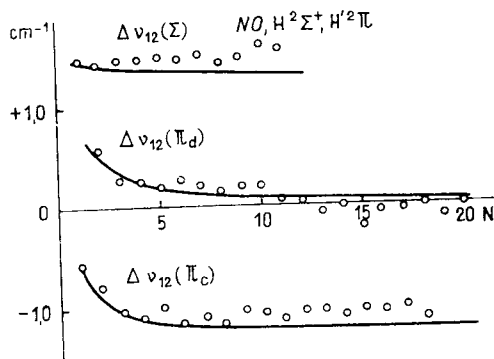


Fig. 2.23 Spin splitting of the d -term complex formed by the terms $H^2\Sigma^+$ and $H'^2\Pi$ of the NO molecule, according to Kovács [114]. In Eq. (13) of the theoretical curve, $A = 0.75 \text{ cm}^{-1}$, $\alpha = 6.9 \text{ cm}^{-1}$. In fact, formula (13) can be called spin splitting only for the ${}^2\Pi$ terms, but not for the ${}^2\Sigma$ terms. With respect to the latter, the actual spin splitting shows a small deviation from the theoretical curve; this can be eliminated by (2.1.3-16) with the value $\gamma = 0.022 \text{ cm}^{-1}$.

$$\begin{aligned}\Delta\nu_{12}(^2\Pi_d) &= \frac{A(N + 1/2)}{N(N + 1)} \\ \Delta\nu_{12}(^2\Pi_c) &= \left\{ \frac{N + 1/2 + \sigma}{2N(N + 1)} - \sqrt{3} \right\} A \\ \Delta\nu_{12}(^2\Sigma) &= \left\{ \frac{N + 1/2 - \sigma}{2N(N + 1)} + \sqrt{3} \right\} A\end{aligned}\tag{13}$$

where

$$\sigma = \frac{\alpha - 2}{4\sqrt{3N(N + 1)}} (N + 1/2)\tag{14}$$

Applying Formula (13) to the $H^2\Sigma^+$ and $H'^2\Pi$ term complex of the NO molecule yields a good agreement with experimental results (Fig. 2.23)

INTENSITY DISTRIBUTION IN ROTATIONAL BANDS

The singlet and multiplet terms discussed so far describe the possible excited states of the molecules. The transitions among these states produce the observed spectral lines. These transitions determine the *wave numbers* of the observed lines, i.e. the position of the lines within the spectrum. The wave number is one of the most characteristic features of a spectral line. Not all the transitions indicated as possible by the term differences will, however, occur in reality. This raises the problem: which transitions lead to actual spectral lines. It was in answer to this problem that the *selection rules* were formulated. (See Introduction.)

The spectral lines are, however, characterized not only by their position within the spectrum, but also by their *intensity* or strength. In other words, if the transition producing the line in question is admitted by the selection rules, the problem that emerges is the probability of the transition. These topics will be dealt with subsequently.

3.1. GENERAL REMARKS

(a) Theoretical Introduction. The *intensity* of a spectral line *in emission* is the energy per unit time that is emitted by the light source emitting the line in all directions of space. If $N_{n',v',J'}$ is the number of molecules in the initial state and if $A_{n''v''J''}^{n'v'J'}$ is the *transition probability introduced by Einstein for spontaneous emission*, i.e. the fraction of molecules performing in unit time the transition from the initial state $n'v'J'$ to the state $n''v''J''$, then the emission intensity is

$$I_{n''v''J''}^{n'v'J'} = N_{n',v',J'} h c \nu A_{n''v''J''}^{n'v'J'} \quad (1)$$

where J is the rotational quantum number, v is the vibrational quantum number, and n represents the remainder of the quantum numbers, not written explicitly, of the electronic state in question; h is *Planck's constant*, c is the velocity of light in vacuum, and ν is the wave number of the spectral line emitted in the transition. According to wave mechanics, $A_{n''v''J''}^{n'v'J'}$ is related to the matrix element R of the di-pole moment of the molecule by

$$A_{n''v''J''}^{n'v'J'} = \frac{64\pi^4 \nu^3}{3h} \frac{\sum |R_{n''v''J''}^{n'v'J'}|^2}{g_{J'}} \quad (2)$$

where $g_{J'}$ is the degree of degeneracy of the initial state (which in the present case is the higher-energy state) and the summation is to be extended over all possible combinations of the sub-levels of the upper states with those of the lower states (cf. the subsequent discussion).

For thin layers (whose thickness we shall denote Δx), if ϱ is the radiation density of the incident radiation of wave number ν , then the intensity of *absorption*, i.e. the energy absorbed in unit time from an incident beam of 1 cm^2 cross-section, is given by

$$I_{n''v''J''}^{n'v'J'} = N_{n''v''J''} h\nu\varrho\Delta x B_{n''v''J''}^{n'v'J'} \quad (3)$$

where $N_{n''v''J''}$ is the number of molecules per cm^3 in the initial state $n''v''J''$ (the lower-energy state in the present case), and $B_{n''v''J''}^{n'v'J'}$ is the *Einstein transition probability of absorption*, for which wave mechanics yields

$$B_{n''v''J''}^{n'v'J'} = \frac{8\pi^3}{3h^2c} \frac{\sum |R_{n''v''J''}^{n'v'J'}|^2}{g_{J''}} \quad (4)$$

where $g_{J''}$ means the degree of degeneracy of the initial state. Since the resultant angular momentum J of the molecule can be oriented in $2J + 1$ ways in the presence of an external magnetic field, each of the rotational levels is $(2J + 1)$ -fold degenerate. Hence, for emission, $g_{J'} = 2J' + 1$, whereas for absorption, $g_{J''} = 2J'' + 1$, and, furthermore, the summation is to be extended over all possible combinations of the magnetic quantum numbers M' and M'' for the two states involved in the transition.

If it is assumed that, in a first approximation, the electronic motion and the vibration and rotation of the nuclei do not influence each other, then the di-pole moment of the molecule can be written as

$$\begin{aligned} R_{n''v''J''}^{n'v'J'} &= \int \psi_a^* \mathbf{M} \psi_a d\tau = \int \Phi_n^* R_v^* u_{J',\Omega',M'}^* (\mathbf{M}_e + \mathbf{M}_n) \Phi_n R_v u_{J'',\Omega'',M''} d\tau \\ &= \int \Phi_n^* \mathbf{M}_e \Phi_n R_v^* R_v u_{J',\Omega',M'}^* u_{J'',\Omega'',M''} d\tau + \\ &+ \int \Phi_n^* \Phi_n d\tau_e \int R_v^* u_{J',\Omega',M'}^* \mathbf{M}_n R_v u_{J'',\Omega'',M''} d\tau_n \end{aligned} \quad (5)$$

where \mathbf{M} is the operator of vector of the electric moment. Its components in the space-fixed coordinate system are $\mathbf{M}_x = \sum_i e_i x_i$, $\mathbf{M}_y = \sum_i e_i y_i$, $\mathbf{M}_z = \sum_i e_i z_i$. The operator of the vector of the electric moment can be resolved in two parts: $\mathbf{M} = \mathbf{M}_e + \mathbf{M}_n$; here, \mathbf{M}_e does not depend on the internuclear distance, whereas \mathbf{M}_n depends on nothing else; ψ_a is the eigenfunction corresponding to *Hund's* case a , which is obtained by (1.1-23) as the product of the eigenfunctions of electronic motion and nuclear vibration and rotation under the assumption of the mutual independence of these motions. Furthermore, $d\tau = d\tau_e d\tau_n$ where $d\tau_e$ is the volume element of the electron coordinates, and $d\tau_n = r^2 \sin \theta d\theta d\phi dr$ is the volume element of the nuclear coordinates. Since in (5) the electronic eigenfunctions belong

to different electronic states and since they are mutually orthogonal, the second term in (5) disappears.

Dropping the suffix e of \mathbf{M} in the remaining part of (5) and introducing the components

$$R_x = \int \psi_a^* \mathbf{M}_x \psi_a d\tau; \quad R_y = \int \psi_a^* \mathbf{M}_y \psi_a d\tau; \quad R_z = \int \psi_a^* \mathbf{M}_z \psi_a d\tau \quad (6)$$

of the matrix $R_{n''v''j''}^{n'v'j'}$ we can write

$$\sum_{M'M''} |R_{n''v''j''}^{n'v'j'}|^2 = \sum_{M'M''} [|R_x|^2 + |R_y|^2 + |R_z|^2] \quad (7)$$

Reiche and Rademacher [189] found that, of the above expressions, $R_x \neq 0$, $R_y \neq 0$ only if $\Delta M = \pm 1$, whereas $R_z \neq 0$ if $\Delta M = 0$. Of these selection rules, the validity of $\Delta M = 0$ is apparent from R_z in Formula (10) given subsequently and also from the rotational eigenfunction u in Formula (1.1-29). Since (10) contains ω only in u (in the form $\exp(iM\omega)$), it is clear that integration with respect to ω gives a non-zero result only if $M' = M''$. Furthermore, by (1.1-2), in the expression of $R_x \pm iR_y$ a factor $e^{\pm i\omega}$ occurs in addition to the factors $\exp(iM\omega)$ of the eigenfunctions u , and this yields the selection rule $\Delta M = \pm 1$ on integration with respect to ω . This is the first selection rule which in our case means that the summation with respect to M'' can be neglected for emission, whereas the summation with respect to M' can be neglected for absorption.

Further examinations (Landau [146]) have shown that

$$\sum_M |R_{n''v''j''}^{n'v'j'}|^2 = 3 \sum_M |R_z|^2 \quad (8)$$

where, for emission, $M = M'$ and M can vary from $-J'$ to $+J'$, and for absorption $M = M''$ and M can assume the values $-J'', \dots, +J''$. By (8), therefore, it is enough to study the component R_z in the absence of an external magnetic field, and neglecting polarization.

Since, by (1.1-2), \mathbf{M}_z expressed in terms of its components in the molecule-fixed system is

$$\mathbf{M}_z = \mathbf{M}_\eta \sin \theta + \mathbf{M}_\zeta \cos \theta \quad (9)$$

we have

$$\begin{aligned} R_z = & \left\{ \int \overline{\Phi_n^* \mathbf{M}_\eta \Phi_{n'}} d\tau_e \int u_{j'',\Omega',M}^* u_{j'',\Omega'',M} \sin^2 \theta d\theta d\omega + \right. \\ & \left. + \int \overline{\Phi_n^* \mathbf{M}_\zeta \Phi_{n'}} d\tau_e \int u_{j'',\Omega',M}^* u_{j'',\Omega'',M} \sin \theta \cos \theta d\theta d\omega \right\} \int R_e R_{e'} r^2 dr \quad (10) \end{aligned}$$

Since the rotational eigenfunctions $u_{j\Omega M}$ and the components \mathbf{M}_η , \mathbf{M}_ζ do not depend on the inter-nuclear distance r , and since the change of the

electronic eigenfunctions Φ_n vs. r is usually slow, after averaging over r the corresponding integral can be separated from the *overlap integral*:

$$R_{\text{vibr}}^{v'v''} = \int R_e R_{e''} r^2 dr \quad (11)$$

(*Franck-Condon principle*). The square of (11) is proportional to the *band strength*. The integrals connected with the electronic eigenfunctions are the η and ζ components of the *electric transition moment*

$$R_e^{n'n''} = \int \Phi_n^* \mathbf{M} \Phi_{n''} d\tau_e \quad (12)$$

for which the selection rules $\Delta\Sigma = 0$, $\Delta S = 0$ are valid, since \mathbf{M} does not depend on the spin, and the spin-dependent parts of the electronic eigenfunctions are orthogonal. The square of (12) is proportional to the *electronic transition probability*.

The integrals relating to the rotational coordinates in (10) can be written in the form

$$L_{J''\Omega''M}^{J'\Omega'M} = \int u_{J',\Omega',M}^* u_{J'',\Omega'',M} \sin \theta \frac{\cos \theta}{\sin \theta} d\theta d\omega \quad (13)$$

As can be shown the selection rule relating to these integrals is $\Delta\Omega = 0, \pm 1$; more specifically, $\Delta\Omega = 0$ holds for the expression having $\cos \theta$, and $\Delta\Omega = \pm 1$ holds for the one having $\sin \theta$ in the place of the alternative trigonometric function. Since, however, as previously mentioned, the selection rule $\Delta\Sigma = 0$ also holds, the above relations are equivalent to the selection rule $\Delta A = 0, \pm 1$. This means that, for any electronic transition, only one term of expression (10) can be other than zero.

It can further be shown that for (13) the selection rule $\Delta J = 0, \pm 1$ also holds. The *series* of such lines as correspond to the transitions $\Delta\bar{J} = 0$ is called the *Q branch*, whereas those for which $\Delta J = -1$ or $+1$ holds are called *P* or *R branches*, respectively.

Summing the square of the absolute value of (13) over the possible values of the magnetic quantum number and multiplying by 3, we obtain an expression called *line strength*:

$$S_{J'J''} = \sum_{M=-J}^{+J} |R_{\text{rot}}^{J'J''}|^2 = 3 \sum_{M=-J}^{+J} |L_{J''\Omega''M}^{J'\Omega'M}|^2 \quad (14)$$

in which $J = J'$ for emission and $J = J''$ for absorption.

In view of the foregoing considerations, therefore, we obtain for (7) or (8)

$$\sum_M |R_{n''v''J''}^{n'v'J'}|^2 = |R_e^{n'n''}|^2 |R_{\text{vibr}}^{v'v''}|^2 S_{J'J''} \quad (15)$$

with

$$|R_e^{n'n''}|^2 = \left[\delta_{S', S''} \delta_{A', A''} \left| \int \Phi_{n', A', S'}^* \mathbf{M}_e \Phi_{n'', A'', S''} d\tau_e \right|^2 + \right. \\ \left. + \delta_{S', S''} \delta_{A', A' \pm 1} \left| \int \Phi_{n', A', S'}^* \mathbf{M}_q \Phi_{n'', A'', S''} d\tau \right|^2 \right] (2S + 1)^{-1} \quad (16)$$

where $S = S'$ for emission and $S = S''$ for absorption, and the remainder is to be taken from (11) and (14). Accordingly, the expression (15) will enter into (2) and (4) and, *via* these latter, also into (1) and (3) [192].

Let us now deal briefly with the number of molecules in the initial state. It is given by the approximate expression

$$N_{n', v', J'} = \frac{N}{Q} (2 - \delta_{0, A'}) (2J' + 1) e^{-(T_{n'} + G_{v'} + F_{J'})hc/kT} \quad (17)$$

where N is the total number of molecules, $T_{n'}$ is the electronic term, $G_{v'}$ is the vibrational term, $F_{J'}$ is the rotational term for the multiplet components, k is the *Boltzmann* constant, T is absolute temperature, Q is the partition function, whereas in the factor $(2 - \delta_{0, A'})$, due to A -type splitting, $\delta_{0, A'} = 1$ if $A' = 0$; otherwise $\delta_{0, A'} = 0$.

For heteronuclear molecules, the partition function Q is in a rough first approximation,

$$Q = Q_{\text{el}} Q_{\text{vibr}} Q_{\text{rot}} = \frac{\sum_{n', A', S'} (2 - \delta_{0, A'}) (2S' + 1) e^{-hcT_{n'}/kT} kT}{(1 - e^{-hc\omega/kT}) hcB} \quad (18)$$

where ω and B are the average vibrational and rotational constants, respectively, taken to be equal for all electronic terms.

By the above consideration, expression (1), i.e. the intensity of an emission line, can be written

$$I_{n'' v'' J''}^{n' v' J'} = C |R_e^{n'n''}|^2 |R_{\text{vibr}}^{v' v''}|^2 S_{J' J''} e^{-hcF_{J'}/kT} \quad (19)$$

where

$$C = 64/3\pi^4 c v^4 \frac{N}{Q} (2 - \delta_{0, \bar{A}}) e^{-hc(T_{n'} + G_{v'})/kT} \quad (20)$$

which can be regarded as constant at a given temperature within a particular band. Here \bar{A} means the least of the A 's of the states taking part in the transition. Otherwise in the case of heteronuclear molecules, when both A 's are greater than zero, the intensity given by (19) is distributed half-and-half between the components of the A -type doubling.

Since in (19) all factors can be regarded as constant to a good approximation within a band—except for the *Boltzmann* factor, written up explicitly, and the line strength $S_{J' J''}$ —the intensities of the spectral lines within

a band depend, once the *Boltzmann* factor has been taken care of, *only on the line strength*. In other words, the relative intensities of the individual lines of a band arising from a multiplet transition are determined, apart from the *Boltzmann* factor, by the line strength; it is this latter that characterizes the intensity distribution among the branches. The theoretical prediction of these line strengths is therefore of considerable importance. The subject of the present chapter is to provide a theoretical basis for computing *line strengths* for the various possible transitions admitted by the selection rules.

Intensity distribution includes many phenomena that will not be dealt with here, e.g. the dependence of intensity distribution on excitation, intensity alternations in homonuclear molecules, the intensity of *Zeeman* components, and other anomalies. For these subjects, the reader is referred to the well-known, excellent book of Herzberg [4].

(b) Principles of Application to Measured Data. There are three usual ways of application:

(i) In simpler cases (19) is rewritten to read

$$\ln \frac{I_{n''v''J''}^{n'v'J'}}{S_{J'J''}} = -\frac{hcF_{J'}}{kT} + \text{const.} \quad (21)$$

and the left-hand side of this equation is plotted vs. $J(J+1)$. Since in simpler cases $F_{J'}$ is proportional to $J(J+1)$, the plot is (provided the value of $S_{J'J''}$ is correct) a straight line whose slope is a function of temperature (Ornstein and van Wijk [173]).

(ii) In more complicated cases of emission, one adds together the intensities of the lines which belong to the upper states of the same rotational quantum number of the individual multiplet components. It can be shown that in this case $\sum_{J''} S_{J'J''} = 2J' + 1$, whence

$$\ln \sum_{J''} \frac{I_{n''v''J''}^{n'v'J'}}{2J' + 1} = -\frac{hcF_{J'}}{kT} + \text{const.} \quad (22)$$

The temperature can be calculated similarly as in the previous case. The value of the *Boltzmann* factor can then be obtained, and the expression

$$I_{n''v''J''}^{n'v'J'}(J)/e^{-hcF_{J'}/kT} = \text{const. } S_{J'J''} \quad (23)$$

can be formed: it permits the comparison of experimentally determined line strength data with the theoretically calculated ones (Nolan and Jenkins [171]).

(iii) The third method requires the forming of relative intensities of the individual multiplet components:

$$\frac{I_{n''v''J''}^{n'v'J'}}{\sum_{J''} I_{n''v''J''}^{n'v'J'}} = \frac{S_{J'J''}}{\sum_{J''} S_{J'J''}} \quad (24)$$

from which, first of all, the *Boltzmann* factor is absent and, on the other hand, if we refrain from making use of the sum rule ($\sum_{J'} S_{J'J''} = 2J' + 1$) then, in some cases, the complicated $C(J)$ factors (see below) can also be eliminated from the denominators of the factor $S_{J'J''}$ (Fujioka [54]).

In the experimental examples given to illustrate the theoretical discussion of the transitions, the comparison of measurements with theoretical values is based on the above methods.

3.2. INTENSITY DISTRIBUTION AMONG SPIN MULTIPLETS OF THE SAME MULTIPLICITY

The intensities or line strengths calculated from (3.1-19) and (3.1-14) agree with the experimental findings only if all terms in the transitions belong to *Hund's case a*. This is understandable inasmuch as the case *a* eigenfunctions were used to derive Formula (3.1-5) in the first place. Many authors have dealt with the establishment of line strength, e.g. Hönl and London [78], Dennison [40], Reiche [188], Kronig [134], Kronig and Rabi [138], Rademacher and Reiche [184], Hill and van Vleck [77], and Mulliken [155]. They are given in their general form in Table 3.1.

Table 3.1. Line Strengths for *Hund's Case a* in General Form

Branches	Line strengths	Branches		Line strengths
$\Delta A = 0$	${}^{2S+1}X_Q - {}^{2S+1}X_Q$	$\Delta A = +1$	$\Delta A = -1$	${}^{2S+1}X_{Q'} - {}^{2S+1}Y_{Q'}$
$P(J)$	$\frac{J^2 - \Omega^2}{J}$	$P(J)$	$R(J-1)$	$\frac{(J - \Omega - 1)(J - \Omega)}{2J}$
$Q(J)$	$\frac{\Omega^2(2J+1)}{J(J+1)}$	$Q(J)$	$Q(J)$	$\frac{(J+\Omega+1)(J-\Omega)(2J+1)}{2J(J+1)}$
$R(J)$	$\frac{(J+1)^2 - \Omega^2}{J+1}$	$R(J)$	$P(J+1)$	$\frac{(J+\Omega+1)(J+\Omega+2)}{2(J+1)}$

The substitution of the appropriate Ω value yields the case *a* line strengths for transitions of any type and multiplicity. In the line strength columns, Ω always means the smaller of the two Ω 's involved in the transition.

Since in the case of multiplet terms the Σ terms always belong to case *b* and most of the other terms belong to the intermediate case, in rigorous calculations we have to use the intermediate-case eigenfunctions instead of the eigenfunctions ψ_a . By (1.5-4), these can be expressed as linear combinations of the case *a* eigenfunctions:

$$\psi_N = \sum_{\Sigma=-S}^{+S} S_{\Lambda+\Sigma, N} \psi_a^{A+\Sigma} \quad (1)$$

where the coefficients $S_{A+\Sigma, N}$ are the transformation-matrix elements calculated from Formula (1.5-9); their explicit forms have been given in Chapter 2 up to, and including, quartet terms.

For the z component of the electric di-pole moment, (1) yields

$$R_z^{N'N''} = \int \psi_{N'}^* \mathbf{M}_z \psi_{N''} d\tau \quad (2)$$

and finally, for the intensity an expression of the same form as (3.1-19) is obtained with the difference that instead of $S_{J'J''}$ this expression contains

$$S_{N'N''}^{J'J''} = \left| \sum_{\Sigma=-S}^{+S} S_{A'+\Sigma, N'}^{J'J''} \sqrt{3 \sum_{M=-J}^{+J} |L_{J''A''+\Sigma, M}^{J'A'+\Sigma, M}|^2 S_{A''+\Sigma, N''}^{J'J''}} \right|^2 \quad (3)$$

where, in the summation, $J = J'$ for emission and $J = J''$ for absorption, as before. If in Formula (3) the transformation-matrix elements are written in their case b forms, a new selection rule emerges: $\Delta N = 0, \pm 1$. In the present section the explicit intermediate-case forms of (3) will be given for different types of transitions of the same multiplicity up to, and including, triplet terms; for terms of higher multiplicity, the explicit forms will be given for the limiting cases.

3.2.1. Singlet Transitions

For completeness, we shall deal first with singlet transitions. According to the selection rules given in Section 3.1, transitions can occur only between terms for which $\Delta A = 0$ or ± 1 . Putting $\Omega = A$ we obtain from Table 3.1 for the line strengths the results given in Table 3.2.

Table 3.2. Line Strengths
of Singlet Transitions for $\Delta A = 0$

Branches	Line strengths
	${}^1X \rightarrow {}^1X$
$P(J)$	$\frac{(J+A)(J-A)}{J}$
$Q(J)$	$\frac{A^2(2J+1)}{J(J+1)}$
$R(J)$	$\frac{(J+A+1)(J-A+1)}{J+1}$

On the substitution of $A = 0, 1, 2, \dots$, the formulas above yield the line strengths for the transitions ${}^1\Sigma \rightarrow {}^1\Sigma$, ${}^1\Pi \rightarrow {}^1\Pi$, ${}^1A \rightarrow {}^1A$, respectively.

The theoretical considerations in Section 3.1 have referred to the case of *electric di-pole radiation*: accordingly, the selection rules given there hold only for that case. In some molecules, however, deviations from the selection rules in question are observed so it has become necessary to examine also the *electric quadrupole* and *magnetic di-pole radiations*. It has been found that, in the former case, the selection rules valid for J are different and lead to transitions that are 'forbidden' in an electric di-pole radiation. According to Chiu [36], the corresponding line strengths are those given in Table 3.3. The quantity ϱ in this table means the ratio of the vibrational matrix elements: it can be regarded as constant within a particular band. The symbol Π^\pm refers to the two components of opposite symmetry of the A -type doubling.

Table 3.3. Line Strengths for Electric Quadrupole Radiation

Branches	Line strengths	
	${}^1\Sigma \rightarrow {}^1\Sigma$	${}^1\Pi^\pm \rightarrow {}^1\Pi$
$O(J)$	$\frac{J(J-1)}{2J-1}$	$\frac{(1 \pm \varrho)^2}{6} \frac{(J-2)(J+1)}{2J-1}$
$P(J)$	0	$\frac{(1 \mp \varrho J)^2}{6} \frac{2}{J}$
$Q(J)$	$\frac{2J(J+1)(2J+1)}{3(2J-1)(2J+3)}$	$\frac{[3-J(J+1)]^2}{3(2J-1)J(J+1)(2J+3)} + \frac{2(2J+1)}{3(2J-1)J(J+1)(2J+3)} \pm \sqrt{\frac{3}{2}} \varrho J(J+1)^2$
$R(J)$	0	$\frac{[1 + \varrho(J+1)]^2}{6} \frac{2}{J+1}$
$S(J)$	$\frac{(J+1)(J+2)}{2J+3}$	$\frac{(1 \pm \varrho)^2}{6} \frac{J(J+3)}{2J+3}$

In magnetic di-pole radiation, the same branches arise as in electric di-pole radiation, with the same dependence of the line strengths on the rotational quantum number.

The line strength formulas for transitions between electronic states of different type, i.e. for $\Delta A = \pm 1$, are listed in Table 3.4.

Table 3.4. Line Strengths of Singlet Transitions for $\Delta A = \pm 1$

Branches		Line strengths
$\Delta A = +1$	$\Delta A = -1$	${}^1X \rightarrow {}^1Y$
$P(J)$	$R(J-1)$	$\frac{(J-A-1)(J-A)}{2J}$
$Q(J)$	$Q(J)$	$\frac{(J-A)(J+A+1)(2J+1)}{2J(J+1)}$
$R(J)$	$P(J+1)$	$\frac{(J+A+1)(J+A+2)}{2(J+1)}$

Table 3.5. Line Strengths for Electric Quadrupole Radiation

Branches		Line strengths			
$AA=+1$	$AA=-1$	${}^1\Pi-{}^1\Sigma$	${}^1A-{}^1\Sigma$	${}^1A-{}^1\Pi$	${}^1\Phi-{}^1A$
$O(J)$	$S(J-2)$	$\frac{4J(J-2)}{3(2J-1)}$	$\frac{(J-2)(J-3)}{3(2J-1)}$	$\frac{2(J-3)(J-2)(J+1)}{3J(2J-1)}$	$\frac{(J-4)(J-3)(J-2)}{6J(2J-1)}$
$P(J)$	$R(J-1)$	$\frac{2(J+1)}{3}$	$\frac{2(J-2)}{3}$	$\frac{(J-2)(J+3)^2}{3J(J+1)}$	$\frac{(J-3)(J-2)(J+2)}{3J(J+1)}$
$Q(J)$	$Q(J)$	$\frac{2(2J+1)}{(2J-1)(2J+3)}$	$\frac{2(J-1)(J+2)(2J+1)}{(2J-1)(2J+3)}$	$\frac{9(J-1)(J+2)(2J+1)(J-2)(J+2)(J+3)(2J+1)}{J(J+1)(2J-1)(2J+3)}$	$\frac{(J-2)(J-1)(J+2)(J+3)(2J+1)}{J(J+1)(2J-1)(2J+3)}$
$R(J)$	$P(J+1)$	$\frac{2J}{3}$	$\frac{2(J+3)}{3}$	$\frac{(J-2)^2(J+3)}{3J(J+1)}$	$\frac{(J-1)(J+3)(J+4)}{3J(J+1)}$
$S(J)$	$O(J+2)$	$\frac{4(J+1)(J+3)}{3(2J+3)}$	$\frac{(J+3)(J+4)}{3(2J+3)}$	$\frac{2J(J+3)(J+4)}{3(J+1)(2J+3)}$	$\frac{(J+3)(J+4)(J+5)}{6(J+1)(2J+3)}$

The quantum number A in Table 3.4 means throughout the smaller of the two A 's involved in the transition. In the notation used here, the branches in the first column of Table 3.4 refer to the transitions ${}^1\Pi \rightarrow {}^1\Sigma$, ${}^1\Delta \rightarrow {}^1\Pi$, ${}^1\Phi \rightarrow {}^1\Delta$, ..., whereas the branches in the second column refer to the transitions ${}^1\Sigma \rightarrow {}^1\Pi$, ${}^1\Pi \rightarrow {}^1\Delta$, ${}^1\Delta \rightarrow {}^1\Phi$,

Similarly as in the previous case, the electric quadrupole radiation leads to the appearance of new branches with different line strengths. These latter are listed in Table 3.5.

The expressions in Table 3.5 are due to Chiu [36]. One of them has been applied to the $a{}^1\Pi \leftarrow X{}^1\Sigma_g^+$ transition of the N_2 molecule. The theoretical results and the observed intensities are compared in Fig. 3.1 after Vanderslice, Wilkinson and Tilford [208].

In the case of magnetic di-pole radiation, the line strengths are given by expressions identical with those for electric dipole radiation.

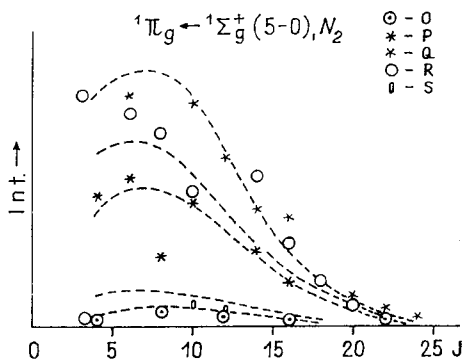


Fig. 3.1 Intensity distribution of the transition $5-0\ a{}^1\Pi_g \leftarrow X{}^1\Sigma_g^+$ in the electric quadrupole radiation of the N_2 molecule, according to Vanderslice, Wilkinson, and Tilford [208]. The procedure of formula (3.1-23) was applied but without division by the Boltzmann factor.

3.2.2. Doublet Transitions

According to the selection rules given in Section 3.1, only transitions with $\Delta A = 0, \pm 1$ can occur also in the doublet case. The line strengths calculated from Table 3.1 agree with the experimental data only for transitions between case a terms. Since, however, the 2Σ terms are always those for case b , and the others generally belong to the intermediate case, Formula (3.2-3) should be used to calculate line strengths, as it is more general than (3.1-14). In order to calculate line strengths from (3.2-3), we require not only the transformation-matrix elements from (2.1.3-5) but also the case a amplitudes from (3.1-14) whose absolute magnitudes are, in fact, the roots listed in Table 3.1: $\sqrt{S_{J'J''}} = q({}^2X_{A+\Sigma}, {}^2X_{A+\Sigma})(J'J'')$.

For doublet transitions with $\Delta A = 0$, these will be as follows:

$$q({}^2X_{A+1/2}, {}^2X_{A+1/2})(J-1, J) = \sqrt{\frac{(J-A-1/2)(J+A+1/2)}{J}} P_2(J)$$

$$q({}^2X_{A-1/2}, {}^2X_{A-1/2})(J-1, J) = \sqrt{\frac{(J-A+1/2)(J+A-1/2)}{J}} P_1(J)$$

$$q(^2X_{A+1/2}, ^2X_{A+1/2})(J, J) = \sqrt{\frac{(A + 1/2)^2 (2J + 1)}{J(J + 1)}} \quad Q_2(J) \quad (1)$$

$$q(^2X_{A-1/2}, ^2X_{A-1/2})(J, J) = \sqrt{\frac{(A - 1/2)^2 (2J + 1)}{J(J + 1)}} \quad Q_1(J)$$

$$q(^2X_{A+1/2}, ^2X_{A+1/2})(J + 1, J) = \sqrt{\frac{(J - A + 1/2)(J + A + 3/2)}{J + 1}} \quad R_2(J)$$

$$q(^2X_{A-1/2}, ^2X_{A-1/2})(J + 1, J) = \sqrt{\frac{(J - A + 3/2)(J + A + 1/2)}{J + 1}} \quad R_1(J)$$

The line strengths calculated by means of the above formulas and the transformation-matrix elements are listed in Table 3.6. Concerning the explicit forms of $u^\pm(J)$ and $C^\pm(J)$, occurring in the table, the reader is referred to (2.1.3-6); in the case of inverted terms, Y is to be substituted with negative sign. From Table 3.6, the line strengths of the transitions $^2\Sigma \rightarrow ^2\Sigma$, $^2\Pi \rightarrow ^2\Pi$, $^2\Delta \rightarrow ^2\Delta$, ... can be obtained by the substitutions $A = 0, 1, 2, \dots$. This general form is reported here for the first time although Mulliken [152, 155] gave general formulas for limiting-case transitions of any type ($^2X(a) \rightarrow ^2X(b)$, $^2X(b) \rightarrow ^2X(b)$). His formulas can be obtained from the line-strength expressions listed in Table 3.6 by putting

$$u^+(J) = 2A(Y - 2); \quad u^-(J) = 0; \quad C^+(J) = 2A^2(Y - 2)^2 \\ C^-(J) = 2(J - A + 1/2)(J + A + 1/2); \quad Y = \infty \quad (2)$$

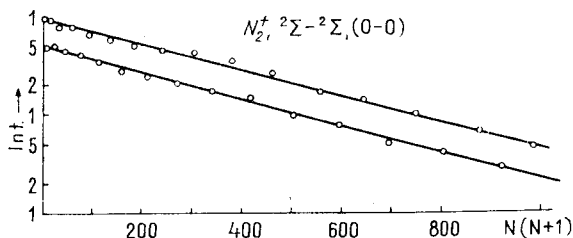


Fig. 3.2 Intensity distribution in the transitions 0-0 $^2\Sigma \rightarrow ^2\Sigma$, of the N_2^+ molecule, according to Ornstein and van Wijk [173]. Since for the transition $^2\Sigma \rightarrow ^2\Sigma$, $S^R \sim J + 1$ and $S^P \sim J$ (where $J = N + 1/2$, $N - 1/2$) by formula (3.1-21) the plots of $\log(I/J + 1)$ and $\log(I/J)$ vs. $J(J + 1)$ or $N(N + 1)$, should give straight lines. For the P and R branches belonging to the same upper N value, the same straight line is obtained within the limits of experimental error. (The two straight lines in the figure are for the intensity alternation arising from the identity of the nuclei.)

Table 3.6. Line Strengths of Doublet Transitions for $\Delta I = 0$ in General Form

Branches	Line strengths
$\Delta A = 0$	${}^2X(\text{int}) - {}^2X(\text{int})$
$P_1(J)$	$\frac{(J - A - 1/2)(J + A + 1/2)}{4JC'-(J-1)C''-(J)} \{u'-(J-1)u''-(J) + 4(J - A + 1/2) \times$ $\times (J + A - 1/2)\}^2$
$Q_1(J)$	$\frac{J + 1/2}{2J(J+1)C'-(J)C''-(J)} \{(A + 1/2)u'-(J)u''-(J) + 4(A - 1/2)(J - A + 1/2) \times$ $\times (J + A + 1/2)\}^2$
$R_1(J)$	$\frac{(J - A + 1/2)(J + A + 3/2)}{4(J+1)C'-(J+1)C''-(J)} \{u'-(J+1)u''-(J) + 4(J - A + 3/2) \times$ $\times (J + A + 1/2)\}^2$
${}^oP_{21}(J)$	$\frac{(J - A - 1/2)(J + A + 1/2)}{4JC'+(J-1)C''-(J)} \{u'+(J-1)u''-(J) - 4(J - A + 1/2) \times$ $\times (J + A - 1/2)\}^2$
${}^RQ_{21}(J)$	$\frac{J + 1/2}{2J(J+1)C'+(J)C''-(J)} \{(A + 1/2)u'+(J)u''-(J) - 4(A - 1/2)(J - A + 1/2) \times$ $\times (J + A + 1/2)\}^2$
${}^sR_{21}(J)$	$\frac{(J - A + 1/2)(J + A + 3/2)}{4(J+1)C'+(J+1)C''-(J)} \{u'+(J+1)u''-(J) - 4(J - A + 3/2) \times$ $\times (J + A + 1/2)\}^2$
${}^oP_{12}(J)$	$\frac{(J - A - 1/2)(J + A + 1/2)}{4JC'-(J-1)C''+(J)} \{u'-(J-1)u''+(J) - 4(J - A + 1/2) \times$ $\times (J + A - 1/2)\}^2$
${}^PQ_{12}(J)$	$\frac{J + 1/2}{2J(J+1)C'-(J)C''+(J)} \{(A + 1/2)u'-(J)u''+(J) - 4(A - 1/2)(J - A + 1/2) \times$ $\times (J + A + 1/2)\}^2$
${}^oR_{12}(J)$	$\frac{(J - A + 1/2)(J + A + 3/2)}{4(J+1)C'-(J+1)C''+(J)} \{u'-(J+1)u''+(J) - 4(J - A + 3/2) \times$ $\times (J + A + 1/2)\}^2$
$P_2(J)$	$\frac{(J - A - 1/2)(J + A + 1/2)}{4JC'+(J-1)C''+(J)} \{u'+(J-1)u''+(J) + 4(J - A + 1/2) \times$ $\times (J + A - 1/2)\}^2$
$Q_2(J)$	$\frac{J + 1/2}{2J(J+1)C'+(J)C''+(J)} \{(A + 1/2)u'+(J)u''+(J) + 4(A - 1/2)(J - A + 1/2) \times$ $\times (J + A + 1/2)\}^2$
$R_2(J)$	$\frac{(J - A + 1/2)(J + A + 3/2)}{4(J+1)C'+(J+1)C''+(J)} \{u'+(J+1)u''+(J) + 4(J - A + 3/2) \times$ $\times (J + A + 1/2)\}^2$

for the case a terms ($Y \gg J(J+1)$) and

$$u^+(J) = 2(J - A + 1/2); \quad u^-(J) = 2(J + A + 1/2)$$

$$C^+(J) = 4(J + 1/2)(J - A + 1/2); \quad C^-(J) = 4(J + 1/2)(J + A + 1/2) \quad (3)$$

for the case b terms ($Y \ll J(J+1)$).

As an experimental application let us present the intensity distribution in the ${}^2\Sigma \rightarrow {}^2\Sigma$ transition (0-0 band) in the 'negative nitrogen bands' of the N_2^+ molecule, as observed by Ornstein and van Wijk [173]. Figure 3.2 shows that the left-hand side of (3.1-21) does indeed give a straight line when plotted vs. $N(N+1)$.

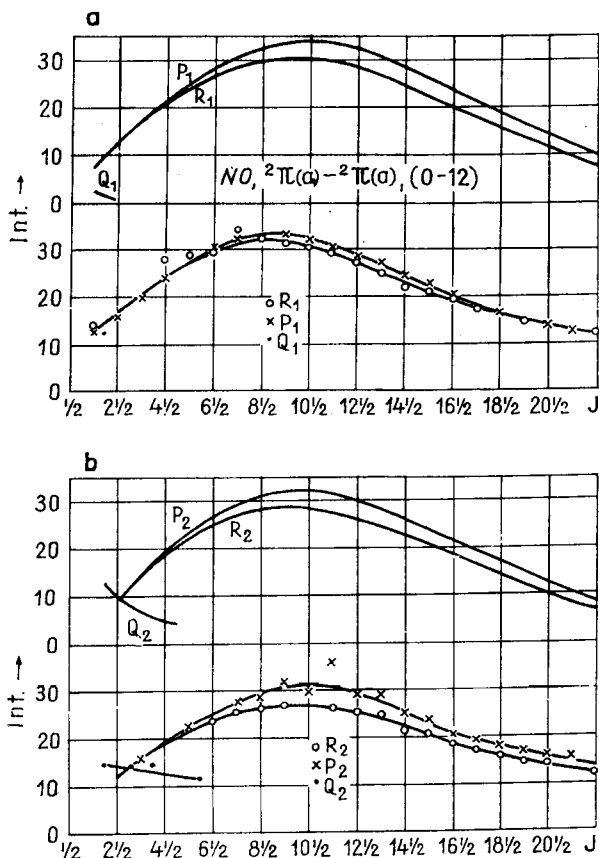


Fig. 3.3 Intensity distribution of the ${}^2\Pi(a) \rightarrow {}^2\Pi(u)$ 0-12 band of the NO molecule, according to Barton, Jenkins, and Mulliken [11]. In each figure, the lower and upper curves represent the observed and calculated intensities, respectively; the result of (3.1-23) is not divided by the Boltzmann factor.

Barton, Jenkins and Mulliken [11] applied the above formulas to the 0-12 band of the transition ${}^2\Pi(a)-{}^2\Pi(a)$ of the β -bands of the NO molecule, using the procedure (3.1-23) but without dividing by the *Boltzmann* factor. This is why the curves of the *P* and *R* branches which otherwise exhibit a monotonic increase with increasing *N* now decrease after having reached a maximum (Fig. 3.3).

By Table 3.1, the absolute magnitude of the case *a* amplitudes for the transitions between terms of different type (with $\Delta A = \pm 1$), are as follows:

$$\Delta A = +1 \quad \Delta A = -1$$

$$q({}^2X_{A'+1/2}, {}^2Y_{A''+1/2})(J-1, J) = \sqrt{\frac{(J-A-3/2)(J-A-1/2)}{2J}} \quad P_2(J) \quad R_2(J-1)$$

$$q({}^2X_{A'-1/2}, {}^2Y_{A''-1/2})(J-1, J) = \sqrt{\frac{(J-A-1/2)(J-A+1/2)}{2J}} \quad P_1(J) \quad R_1(J-1)$$

$$q({}^2X_{A'+1/2}, {}^2Y_{A''+1/2})(J, J) = \sqrt{\frac{(J-A-1/2)(J+A+3/2)(2J+1)}{2J(J+1)}} \quad Q_2(J) \quad Q_2(J)$$

$$q({}^2X_{A'-1/2}, {}^2Y_{A''-1/2})(J, J) = \sqrt{\frac{(J-A+1/2)(J+A+1/2)(2J+1)}{2J(J+1)}} \quad Q_1(J) \quad Q_1(J)$$

$$q({}^2X_{A'+1/2}, {}^2Y_{A''+1/2})(J+1, J) = \sqrt{\frac{(J+A+3/2)(J+A+5/2)}{2(J+1)}} \quad R_2(J) \quad P_2(J+1)$$

$$q({}^2X_{A'-1/2}, {}^2Y_{A''-1/2})(J+1, J) = \sqrt{\frac{(J+A+1/2)(J+A+3/2)}{2(J+1)}} \quad R_1(J) \quad P_1(J+1)$$

The line strengths calculated by the above considerations, making use of the transformation-matrix elements, are listed in Table 3.7, where the explicit *A* values always mean the smaller of the two *A*'s involved in the transition. On the substitution of the appropriate value of *A*, the formulas in the third column give the line strengths of the transition ${}^2\Pi-{}^2\Sigma$, ${}^2\Delta-{}^2\Pi$, ${}^2\Phi-{}^2\Delta$, ... for branches in the first column, and the same for transitions ${}^2\Sigma-{}^2\Pi$, ${}^2\Pi-{}^2\Delta$, ${}^2\Delta-{}^2\Phi$, ... for branches in the second column, with both terms in the intermediate case between *Hund*'s cases *a* and *b*. The formulas valid for the limiting cases can be obtained from those in Table 3.7 by the substitutions (2) and (3). The limiting-case formulas and some expressions for special transitions have long been known. Thus for cases *a* and *b*, formulas valid for ${}^2X(a)-{}^2Y(a)$ and ${}^2X(b)-{}^2Y(b)$ transitions of any type were given by Mulliken [155], for ${}^2\Pi(a)-{}^2\Sigma(b)$ transitions by Hill and van Vleck [77], for ${}^2\Pi(\text{int})-{}^2\Sigma(b)$ transitions by Earls [49]; finally, the formulas for the transitions ${}^2\Delta(b)-{}^2\Pi(a)$ were again given by Hill and van Vleck [77].

The formulas for ${}^2\Pi(a)-{}^2\Sigma(b)$ were compared with experimental data concerning the HgH molecule by Kapuscinski and Eymers [91] and Eymers

Table 3.7. Line Strengths of Doublet Transitions for $\Delta A = \pm 1$ in General Form

Branches		Line strengths
$\Delta A = +1$	$\Delta A = -1$	${}^2X(\text{int}) - {}^2Y(\text{int})$
$P_1(J)$	$R_1(J-1)$	$\frac{(J-A-\frac{3}{2})(J-A-\frac{1}{2})}{8JC'-(J-1)C''-(J)} \{u'-(J-1)u''-(J) + 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
$Q_1(J)$	$Q_1(J)$	$\frac{(J-A-\frac{1}{2})(J+\frac{1}{2})(J+A+\frac{3}{2})}{4J(J+1)C'-(J)C''-(J)} \{u'-(J)u''-(J) + 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
$R_1(J)$	$P_1(J+1)$	$\frac{(J+A+\frac{3}{2})(J+A+\frac{5}{2})}{8(J+1)C'-(J+1)C''-(J)} \{u'-(J+1)u''-(J) + 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
${}^Q P_{21}(J)$	${}^Q R_{12}(J-1)$	$\frac{(J-A-\frac{3}{2})(J-A-\frac{1}{2})}{8JC'+(J-1)C''-(J)} \{u'+(J-1)u''-(J) - 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
${}^R Q_{21}(J)$	${}^P Q_{12}(J)$	$\frac{(J-A-\frac{1}{2})(J+\frac{1}{2})(J+A+\frac{3}{2})}{4J(J+1)C'+(J)C''-(J)} \{u'+(J)u''-(J) - 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
${}^S R_{21}(J)$	${}^O P_{12}(J+1)$	$\frac{(J+A+\frac{3}{2})(J+A+\frac{5}{2})}{8(J+1)C'+(J+1)C''-(J)} \{u'+(J+1)u''-(J) - 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
${}^O P_{12}(J)$	${}^S R_{21}(J-1)$	$\frac{(J-A-\frac{3}{2})(J-A-\frac{1}{2})}{8JC'-(J-1)C''+(J)} \{u'-(J-1)u''+(J) - 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
${}^P Q_{12}(J)$	${}^R Q_{21}(J)$	$\frac{(J-A-\frac{1}{2})(J+\frac{1}{2})(J+A+\frac{3}{2})}{4J(J+1)C'-(J)C''+(J)} \{u'-(J)u''+(J) - 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
${}^Q R_{12}(J)$	${}^Q P_{21}(J+1)$	$\frac{(J+A+\frac{3}{2})(J+A+\frac{5}{2})}{8(J+1)C'-(J+1)C''+(J)} \{u'-(J+1)u''+(J) - 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
$P_2(J)$	$R_2(J-1)$	$\frac{(J-A-\frac{3}{2})(J-A-\frac{1}{2})}{8JC'+(J-1)C''+(J)} \{u'+(J-1)u''+(J) + 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
$Q_2(J)$	$Q_2(J)$	$\frac{(J-A-\frac{1}{2})(J+\frac{1}{2})(J+A+\frac{3}{2})}{4J(J+1)C'+(J)C''+(J)} \{u'+(J)u''+(J) + 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$
$R_2(J)$	$P_2(J+1)$	$\frac{(J+A+\frac{3}{2})(J+A+\frac{5}{2})}{8(J+1)C'+(J+1)C''+(J)} \{u'+(J+1)u''+(J) + 4(J-A+\frac{1}{2})(J+A+\frac{1}{2})\}^2$

[50]. They used procedure (3.1-21) and, as is apparent from Fig. 3.4, they did not obtain a straight line, which in this case may be attributed to two causes. One is that the initial state is not in a *Maxwell-Boltzmann* distribution; the other is that, for the ${}^2\Pi$ state, the intermediate-case formulas should have been applied. The latter were, however, not known at the time of the above publications. Besides, the authors held the view that the discrepancy was due to the cause mentioned first.

The possibility of a further experimental verification exists in the case of the transition ${}^2\Delta-{}^2\Pi$ of the SiH molecule, whose intensities have been measured (Jackson [89]): the data obtained have not yet been compared with the theoretical formulas, however.

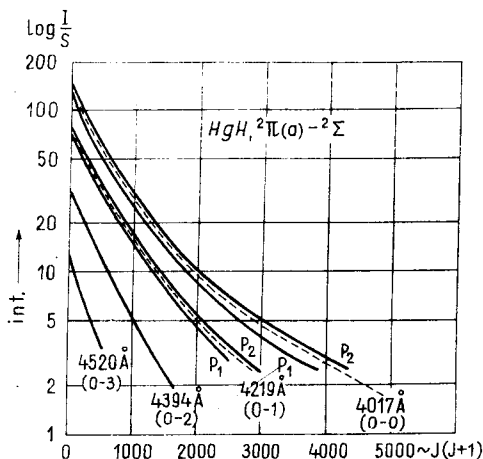


Fig. 3.4 Intensity distribution for different transitions ${}^2\Pi(a)-{}^2\Sigma$ of the HgH molecule, according to Kapuscinski and Eymers [91] using formula (3.1-21). The dashed lines give average of the intensities of Q_1, Q_2, R_1, R_2 branch together; the averages of all the branches in the transitions at 4520 and 4394 Å are shown by single curves.

3.2.3. Triplet Transitions

Similarly as in the case of the doublet transitions, the intermediate-case formulas can be given for $\Delta A = 0$ and ± 1 also in the triplet case. The case a amplitudes can be taken from Table 3.1, and the elements of the transformation matrix from (2.1.4-8). These expressions and (3.2-3) yield the intermediate-case formulas for $\Delta A = 0$ listed in Table 3.8. The expressions for $u_1^\pm(J), u_3^\pm(J), C_1(J), C_2(J), C_3(J)$ in Table 3.8 can be found in (2.1.4-9) and (2.1.4-10). If there are inverted terms among those involved in the transition, then the appropriate Y is to be written with a negative sign; furthermore, $-\Delta$ is to be written instead of Δ in $C_1(J)$ and $C_3(J)$.

From Table 3.8 the line strengths of the transitions ${}^3\Sigma-{}^3\Sigma, {}^3\Pi-{}^3\Pi, {}^3\Delta-{}^3\Delta, \dots$ can be obtained by putting $\Delta = 0, 1, 2, \dots$. The line strengths of some special transitions were already known earlier: those of the transitions ${}^3\Pi(a)-{}^3\Pi(a), {}^3\Pi(a)-{}^3\Pi(b), {}^3\Pi(b)-{}^3\Pi(b)$ were given by Budó [21]; those of the transitions ${}^3\Pi(a)-{}^3\Pi(int), {}^3\Pi(b)-{}^3\Pi(int)$ and those of ${}^3\Delta(a)-{}^3\Delta(a), {}^3\Delta(a)-{}^3\Delta(int), {}^3\Delta(a)-{}^3\Delta(b), {}^3\Delta(int)-{}^3\Delta(int), {}^3\Delta(int)-{}^3\Delta(b), {}^3\Delta(b)-{}^3\Delta(b)$ were given by Kovács [120]. These formulas can be obtained for normal case a terms ($Y > 0$) from Table 3.8, by putting

$$u_1^\pm(J) = u_3^\pm(J) = 2.1(Y - 2); \quad u_1^-(J) = u_3^-(J) = 0$$

Table 3.8. Line Strengths of Triplet Transitions for $\Delta A = 0$ in General Form

Branches $\Delta A = 0$	Line strengths	
	${}^3X(\text{int}) - {}^3X(\text{int})$	
$P_1(J)$	$\frac{(J-A)(J+A)}{16JC_1^2(J-1)C_1^2(J)} \{ (J-A+1)(J+A-1)u_1' + (J-A-1)(J+A+1)u_1'' - (J-1)u_1''' - (J+1)u_1'''' - (J+1)u_1'''' - (J+1)u_1'''' \}$	
$Q_1(J)$	$\frac{2J+1}{16J(J+1)C_1^2(J)C_1^2(J)} \{ (A-1)(J-A+1)(J+A)u_1' + (J+A+1)(J-A+1)(J+A+1)u_1'' - (J+1)u_1''' - (J+1)u_1'''' - (J+1)u_1'''' \}$	
$R_1(J)$	$\frac{(J-A+1)(J+A+1)}{16(J+1)C_1^2(J+1)C_1^2(J)} \{ (J-A+2)(J+A)u_1' + (J+A+1)u_1'' + (J-A)(J+A+2)u_1''' - (J+1)u_1'''' - (J+1)u_1'''' \}$	
${}^Q P_{21}(J)$	$\frac{(J-A)(J+A)}{2JC_1^2(J-1)C_1^2(J)} \{ (J-A+1)(J+A-1)u_1' + (J-A-1)(J+A+1)u_1'' - (J-1)u_1''' - (J+1)u_1'''' - (J+1)u_1'''' \}$	
${}^R Q_{21}(J)$	$\frac{2J+1}{2J(J+1)C_1^2(J)C_1^2(J)} \{ (A-1)(J-A+1)(J+A)u_1' + (J+A+1)u_1'' - (A+1)(J-A)(J+A+1)u_1''' - (J+1)u_1'''' - (J+1)u_1'''' \}$	
$S_{21}(J)$	$\frac{(J-A+1)(J+A+1)}{2(J+1)C_1^2(J+1)C_1^2(J)} \{ (J-A+2)(J+A)u_1' + (J+A+1)u_1'' - (J-A)(J+A+2)u_1''' - (J+1)u_1'''' - (J+1)u_1'''' \}$	
${}^R P_{31}(J)$	$\frac{(J-A)(J+A)}{16JC_1^2(J-1)C_1^2(J)} \{ (J-A+1)(J+A-1)u_1' + (J-A-1)(J+A+1)u_1'' - (J-1)u_1''' - (J+1)u_1'''' - (J+1)u_1'''' \}$	
$S_{31}(J)$	$\frac{2J+1}{16J(J+1)C_1^2(J)C_1^2(J)} \{ (A-1)(J-A+1)(J+A)u_1' + (J+A+1)u_1'' - (A+1)(J-A)(J+A+1)u_1''' - (J+1)u_1'''' - (J+1)u_1'''' \}$	
$T_{31}(J)$	$\frac{(J-A+1)(J+A+1)}{16(J+1)C_1^2(J+1)C_1^2(J)} \{ (J-A+2)(J+A)u_1' + (J+A+1)u_1'' - (J-A)(J+A+2)u_1''' - (J+1)u_1'''' - (J+1)u_1'''' \}$	

$$\begin{aligned}
{}^oP_{12}(J) & \frac{(J-A)(J+A)}{2JC_1'(J-1)C_2''(J)} \{ (J-A+1)(J+A-1)u_1'+(J-1)-(J-A-1)(J+A+1)u_1'-(J-1)- \\
& -2A(J-A-1)(J+A-1)(Y''-2) \}^2 \\
{}^pQ_{12}(J) & \frac{2J+1}{2J(J+1)C_1'(J)C_2''(J)} \{ (A-1)(J-A+1)(J+A)u_1'+(J)-(A+1)(J-A)(J+A+1)u_1'-(J)- \\
& -2A^2(J-A)(J+A)(Y''-2) \}^2 \\
{}^qR_{12}(J) & \frac{(J-A+1)(J+A+1)}{2(J+1)C_1'(J+1)C_2''(J)} \{ (J-A+2)(J+A)u_1'+(J+1)-(J-A)(J+A+2)u_1'-(J+1)- \\
& -2A(J-A+1)(J+A+1)(Y''-2) \}^2 \\
P_2(J) & \frac{4(J-A)(J+A)}{JC_2'(J-1)C_2''(J)} \{ \frac{1}{2}A^2(Y'-2)(Y''-2)+(J-A-1)(J+A+1)+(J-A+1)(J+A-1) \}^2 \\
Q_2(J) & \frac{4(2J+1)}{J(J+1)C_2'(J)C_2''(J)} \{ \frac{1}{2}A^3(Y'-2)(Y''-2)+(A+1)(J-A)(J+A+1)+(A-1)(J-A+1)(J+A) \}^2 \\
R_2(J) & \frac{4(J-A+1)(J+A+1)}{(J+1)C_2'(J+1)C_2''(J)} \{ \frac{1}{2}A^2(Y'-2)(Y''-2)+(J-A)(J+A+2)+(J-A+2)(J+A) \}^2 \\
{}^qP_{32}(J) & \frac{(J-A)(J+A)}{2JC_3'(J-1)C_2''(J)} \{ (J-A+1)(J+A-1)u_3'+(J-1)-(J-A-1)(J+A+1)u_3'+(J-1)+ \\
& +2A(J-A)(J+A)(Y''-2) \}^2 \\
{}^RQ_{32}(J) & \frac{2J+1}{2J(J+1)C_3'(J)C_2''(J)} \{ (A-1)(J-A+1)(J+A)u_3'+(J)-(A+1)(J-A)(J+A+1)u_3'+(J)+ \\
& +2A^2(J-A+1)(J+A+1)(Y''-2) \}^2 \\
{}^sR_{32}(J) & \frac{(J-A+1)(J+A+1)}{2(J+1)C_3'(J+1)C_2''(J)} \{ (J-A+2)(J+A)u_3'+(J+1)-(J-A)(J+A+2)u_3'+(J+1)+ \\
& +2A(J-A+2)(J+A+2)(Y''-2) \}^2
\end{aligned}$$

Table 3.8 (continued)

Branches $\Delta A = 0$	Line strengths	
	${}^3X(\text{int})$	${}^3X(\text{int})$
${}^N P_{13}(J)$	$\frac{(J-A)(J+A)}{16JC_1'(J-1)C_3''(J)} \{ (J-A+1)(J+A-1)u_1''-(J)+(J-A-1)(J+A+1)u_1'-(J-1)u_3''+(J) - 8(J-A-1)(J-A+1)(J+A-1)(J+A+1) \}^2$	
${}^O Q_{13}(J)$	$\frac{2J+1}{16J(J+1)C_1'(J)C_3''(J)} \{ (A-1)(J-A+1)(J+A)u_1''-(J)+(A+1)(J-A)(J+A+1)u_1'-(J)u_3''+(J) - 8A(J-A)(J-A+1)(J+A)(J+A+1) \}^2$	
${}^P R_{13}(J)$	$\frac{(J-A+1)(J+A+1)}{16(J+1)C_1'(J+1)C_3''(J)} \{ (J-A+2)(J+A)u_1''+(J+1)u_3''-(J)+(J-A)(J+A+2)u_1'-(J+1)u_3''+(J) - 8(J-A+1)^2(J+A+1)^2 \}^2$	
${}^O P_{23}(J)$	$\frac{(J-A)(J+A)}{2JC_2'(J-1)C_3''(J)} \{ (J-A+1)(J+A-1)u_3''-(J)-(J-A-1)(J+A+1)u_3''+(J)+ 2A(J-A+1)(J+A+1)(Y'-2) \}^2$	
${}^P Q_{23}(J)$	$\frac{2J+1}{2J(J+1)C_2'(J)C_3''(J)} \{ (A-1)(J-A+1)(J+A)u_3''-(J)-(A+1)(J-A)(J+A+1)u_3''+(J)+ 2A^2(J-A+1)(J+A+1)(Y'-2) \}^2$	
${}^Q R_{23}(J)$	$\frac{(J-A+1)(J+A+1)}{2(J+1)C_2'(J+1)C_3''(J)} \{ (J-A+2)(J+A)u_3''-(J)-(J-A)(J+A+2)u_3''+(J)+ 2A(J-A+1)(J+A+1)(Y'-2) \}^2$	
${}^P_3(J)$	$\frac{(J-A)(J+A)}{16JC_3'(J-1)C_3''(J)} \{ (J-A+1)(J+A-1)u_3''-(J-1)u_3''-(J)+(J-A-1)(J+A+1)u_3'+(J) + 8(J-A)(J-A+1)(J+A)(J+A+1) \}^2$	
${}^Q_3(J)$	$\frac{2J+1}{16J(J+1)C_3'(J)C_3''(J)} \{ (A-1)(J-A+1)(J+A)u_3''-(J)u_3''-(J)+(A+1)(J-A)(J+A+1)u_3''+(J)+ 8A(J-A+1)^2(J+A+1)^2 \}^2$	
${}^R_3(J)$	$\frac{(J-A+1)(J+A+1)}{16(J+1)C_3'(J+1)C_3''(J)} \{ (J-A+2)(J+A)u_3''-(J+1)u_3''-(J)+(J-A)(J+A+2)u_3'+(J+1)u_3''+(J)+ 8(J-A+1)(J-A+2)(J+A+1)(J+A+1) \}^2$	

Table 3.9. Line Strengths for Electric Quadrupole Radiation

Branches		Line strengths		Branches		Line strengths		Branches		Line strengths	
$3\Sigma^+ - 3\Sigma^-$	$3\Sigma^- - 3\Sigma^+$	$3\Sigma^+ - 3\Sigma^+$	$3\Sigma^+ - 3\Sigma^+$	$3\Sigma^+ - 3\Sigma^-$	$3\Sigma^- - 3\Sigma^+$	$3\Sigma^+ - 3\Sigma^+$	$3\Sigma^+ - 3\Sigma^+$	$3\Sigma^+ - 3\Sigma^-$	$3\Sigma^- - 3\Sigma^+$	$3\Sigma^+ - 3\Sigma^+$	$3\Sigma^+ - 3\Sigma^+$
$P_1(J)$	$R_1(J-1)$	0		$^0P_{12}(J)$	$^5R_{21}(J-1)$	$\frac{J(J+2)}{2(2J+1)}$		$^N P_{13}(J)$	$^T R_{31}(J-1)$	0	
$Q_1(J)$	$Q_1(J)$	$\frac{2J(J+1)}{2J+1}$		$^P Q_{12}(J)$	$^R Q_{21}(J)$	0		$^0 Q_{13}(J)$	$^S Q_{31}(J)$	$\frac{1}{2(2J+1)}$	
$R_1(J)$	$P_1(J+1)$	0		$^Q R_{12}(J)$	$^Q P_{21}(J+1)$	$\frac{(J-1)J}{2(2J+1)}$		$^P R_{13}(J)$	$^R P_{31}(J+1)$	0	
$^Q P_{21}(J)$	$^Q R_{13}(J-1)$	$\frac{J(J+1)}{2(2J+3)}$		$^P_2(J)$	$^R_2(J-1)$	0		$^0 P_{23}(J)$	$^S R_{32}(J-1)$	$\frac{J(J+2)}{2(2J+3)}$	
$^R Q_{21}(J)$	$^P Q_{12}(J)$	0		$^Q_2(J)$	$^Q_2(J)$	0		$^P Q_{23}(J)$	$^R Q_{32}(J)$	0	
$^S R_{21}(J)$	$^0 P_{12}(J+1)$	$\frac{(J-1)(J+1)}{2(2J-1)}$		$^R_2(J)$	$^P_2(J+1)$	0		$^Q R_{23}(J)$	$^Q P_{32}(J+1)$	$\frac{J(J+1)}{2(2J-1)}$	
$^R P_{31}(J)$	$^P R_{13}(J-1)$	0		$^Q P_{32}(J)$	$^Q R_{23}(J-1)$	$\frac{(J+1)(J+2)}{2(2J+1)}$		$^P_3(J)$	$^R_3(J-1)$	0	
$^S Q_{31}(J)$	$^0 Q_{13}(J)$	$\frac{1}{2(2J+1)}$		$^R Q_{32}(J)$	$^P Q_{23}(J)$	0		$^Q_3(J)$	$^Q_3(J)$	$\frac{2J(J+1)}{2J+1}$	
$^T R_{31}(J)$	$^N P_{13}(J+1)$	0		$^S R_{32}(J)$	$^0 P_{23}(J+1)$	$\frac{(J-1)(J+1)}{2(2J+1)}$		$^R_3(J)$	$^P_3(J+1)$	0	

Table 3.10. Line Strengths of Triplet Transitions for $\Delta A = \pm 1$ in General Form

Branches		Line strengths
$\Delta A = +1$	$\Delta A = -1$	${}^3X(\text{int}) - {}^3Y(\text{int})$
$P_1(J)$	$R_1(J-1)$	$\frac{(J-A-1)(J-A)}{32JC_1'(J-1)C_1''(J)} \{(J-A+1)(J+A)u_1^{'+}(J-1)u_1^{'+}(J) + (J-A-2)(J+A+1)u_1^{'+}(J-1) \times \\ \times u_1^{'+}(J) + 8(J-A-2)(J-A)(J+A)^2\}^2$
$Q_1(J)$	$Q_1(J)$	$\frac{(J-A)(J+A+1)(2J+1)}{32J(J+1)C_1'(J)C_1''(J)} \{(J-A+1)(J+A)u_1^{'+}(J)u_1^{'+}(J) + (J-A-1)(J+A+2) \times \\ \times u_1^{'+}(J)u_1^{'+}(J) + 8(J-A-1)(J-A)(J+A)(J+A+1)\}^2$
$R_1(J)$	$P_1(J+1)$	$\frac{(J+A+1)(J+A+2)}{32(J+1)C_1'(J+1)C_1''(J)} \{(J-A+1)(J+A)u_1^{'+}(J+1)u_1^{'+}(J) + (J-A)(J+A+3)u_1^{'+}(J+1) \times \\ \times u_1^{'+}(J) + 8(J-A)^2(J+A)(J+A+2)\}^2$
${}^Q P_{12}(J)$	${}^Q R_{12}(J-1)$	$\frac{(J-A-1)(J-A)}{4JC_2'(J-1)C_1''(J)} \{(J-A+1)(J+A)u_1^{'+}(J) - (J-A-2)(J+A+1)u_1^{'+}(J) - \\ - 2(A+1)(J-A)(J+A)(Y'-2)\}^2$
$R_{Q21}(J)$	$P_{Q12}(J)$	$\frac{(J-A)(J+A+1)(2J+1)}{4JC_2'(J+1)C_1'(J)C_1''(J)} \{(J-A+1)(J+A)u_1^{'+}(J) - (J-A-1)(J+A+2)u_1^{'+}(J) - \\ - 2(A+1)(J-A)(J+A)(Y'-2)\}^2$
$S R_{21}(J)$	${}^O P_{12}(J+1)$	$\frac{(J+A+1)(J+A+2)}{4(J+1)C_2'(J+1)C_1'(J)} \{(J-A+1)(J+A)u_1^{'+}(J) - (J-A)(J+A+3)u_1^{'+}(J) - \\ - 2(A+1)(J-A)(J+A)(Y'-2)\}^2$
$R P_{31}(J)$	${}^P R_{13}(J-1)$	$\frac{(J-A-1)(J-A)}{32JC_3'(J-1)C_1'(J)} \{(J-A+1)(J+A)u_3^{'+}(J-1)u_3^{'+}(J) + (J-A-2)(J+A+1)u_3^{'+}(J-1) \times \\ \times u_3^{'+}(J) - 8(J-A-1)(J-A)(J+A)(J+A+1)\}^2$
$S Q_{31}(J)$	${}^O Q_{13}(J)$	$\frac{(J-A)(J+A+1)(2J+1)}{32J(J+1)C_3'(J)C_1'(J)} \{(J-A+1)(J+A)u_3^{'+}(J)u_3^{'+}(J) + (J-A-1)(J+A+2) \times \\ \times u_3^{'+}(J)u_3^{'+}(J) - 8(J-A)^2(J+A)(J+A+2)\}^2$
${}^T R_{31}(J)$	${}^N P_{13}(J+1)$	$\frac{(J+A+1)(J+A+2)}{32(J+1)C'(J+1)C''(J)} \{(J-A+1)(J+A)u_3^{'+}(J+1)u_3^{'+}(J) + (J-A)(J+A+3)u_3^{'+}(J+1) \times \\ \times u_3^{'+}(J) - 8(J-A)(J-A+1)(J+A)(J+A+3)\}^2$

${}^oP_{12}(J)$	${}^sR_{21}(J-1)$	$\frac{(J-A-1)(J-A)}{4JC_1'(J-1)C_2''(J)}\{(J-A+1)(J+A)u_1'+(J-1)-(J-A-2)(J+A+1)u_1'-(J-1)-2A(J-A-2)(J+A)(Y''-2)\}^2$
${}^pQ_{12}(J)$	${}^kQ_{21}(J)$	$\frac{(J-A)(J+A+1)(2J+1)}{4J(J+1)C_1'(J)C_2''(J)}\{(J-A+1)(J+A)u_1'+(J)-(J-A-1)(J+A+2)u_1'-(J)-2A(J-A-1)(J+A+1)(Y''-2)\}^2$
${}^oQ_{R_{12}}(J)$	${}^oQ_{P_{21}}(J+1)$	$\frac{(J+A+1)(J+A+2)}{4(J+1)C_1'(J+1)C_2''(J)}\{(J-A+1)(J+A)u_1'+(J+1)-(J-A)(J+A+3)u_1'-(J+1)-2A(J-A)(J+A+2)(Y''-2)\}^2$
${}^P_2(J)$	${}^R_2(J-1)$	$\frac{2(J-A-1)(J-A)}{JC_2''(J-1)C_2''(J)}\{\frac{1}{2}A(A+1)(Y'-2)(Y''-2)+(J-A+1)(J+A)+ (J-A-2)(J+A+1)\}^2$
${}^Q_2(J)$	${}^Q_2(J)$	$\frac{2(J-A)(J+A+1)(2J+1)}{J(J+1)C_2''(J)C_2''(J)}\{\frac{1}{2}A(A+1)(Y'-2)(Y''-2)+(J-A+1)(J+A)+ (J-A-1)(J+A+2)\}^2$
${}^R_2(J)$	${}^P_2(J+1)$	$\frac{2(J+A+1)(J+A+2)}{(J+1)C_2''(J+1)C_2''(J)}\{\frac{1}{2}A(A+1)(Y'-2)(Y''-2)+(J-A+1)(J+A)+ (J-A)(J+A+3)\}^2$
${}^oQ_{P_{32}}(J)$	${}^oQ_{R_{23}}(J-1)$	$\frac{(J-A-1)(J-A)}{4JC_3''(J-1)C_2''(J)}\{(J-A+1)(J+A)u_3'-(J-1)-(J-A-2)(J+A+1)u_3'-(J-1)+2A(J-A-1)(J+A+1)(Y''-2)\}^2$
${}^kQ_{Q_{32}}(J)$	${}^pQ_{Q_{23}}(J)$	$\frac{(J-A)(J+A+1)(2J+1)}{4J(J+1)C_3''(J)C_2''(J)}\{(J-A+1)(J+A)u_3'-(J-A-1)(J+A+2)u_3'-(J)+2A(J-A)(J+A+2)(Y''-2)\}^2$
${}^sR_{32}(J)$	${}^oP_{23}(J+1)$	$\frac{(J+A+1)(J+A+2)}{4(J+1)C_3''(J+1)C_2''(J)}\{(J-A+1)(J+A)u_3'-(J+1)-(J-A)(J+A+3)u_3'-(J+1)+2A(J-A+1)(J+A+3)(Y''-2)\}^2$

Table 3.10 (continued)

Branches		Line strengths
$AA = +1$	$AA = -1$	${}^3X(\text{int}) - {}^3Y(\text{int})$
${}^N P_{13}(J)$	${}^T R_{31}(J-1)$	$\frac{(J-A-1)(J-A)}{32JC_1'(J-1)C_3''(J)} \{ (J-A+1)(J+A)u_1' + (J-1)u_3'' - (J) + (J-A-2)(J+A+1)u_1' - (J-1) \times$ $\times u_3'' + (J) - 8(J-A-2)(J-A+1)(J+A+1)(J+A+1) \}^2$
${}^O Q_{13}(J)$	${}^S Q_{31}(J)$	$\frac{(J-A)(J+A+1)(2J+1)}{32J(J+1)C_1'(J)C_3''(J)} \{ (J-A+1)(J+A)u_1' + (J)u_3'' - (J) + (J-A-1)(J+A+2) -$ $\times u_1' - (J)u_3'' + (J) - 8(J-A-1)(J-A+1)(J+A+1)(J+A+1) \}^2$
${}^P R_{13}(J)$	${}^R P_{31}(J+1)$	$\frac{(J+A+1)(J+A+2)}{32(J+1)C_1'(J+1)C_3''(J)} \{ (J-A+1)(J+A)u_1' + (J+1)u_3'' - (J) + (J-A)(J+A+3) \times$ $\times u_1' - (J+1)u_3'' + (J) - 8(J-A)(J-A+1)(J+A+1)(J+A+1)(J+A+2) \}^2$
${}^O P_{13}(J)$	${}^S R_{32}(J-1)$	$\frac{(J-A-1)(J-A)}{4JC_2''(J-1)C_3''(J)} \{ (J-A+1)(J+A)u_3'' - (J-A-2)(J+A+1)u_3'' + (J) +$ $+ 2(A+1)(J-A+1)(J+A+1)(Y'-2) \}^2$
${}^P Q_{23}(J)$	${}^R Q_{32}(J)$	$\frac{(J-A)(J+A+1)(2J+1)}{4J(J+1)C_2''(J)C_3''(J)} \{ (J-A+1)(J+A)u_3'' - (J-A-1)(J+A+2)u_3'' + (J) +$ $+ 2(A+1)(J-A+1)(J+A+1)(Y'-2) \}^2$
${}^Q P_{23}(J)$	${}^Q P_{32}(J+1)$	$\frac{(J+A+1)(J+A+2)}{4(J+1)C_2''(J+1)C_3''(J)} \{ (J-A+1)(J+A)u_3'' - (J-A)(J+A+3)u_3'' + (J) +$ $+ 2(A+1)(J-A+1)(J+A+1)(Y'-2) \}^2$
${}^P_3(J)$	${}^R_3(J-1)$	$\frac{(J-A-1)(J-A)}{32JC_3''(J-1)C_3''(J)} \{ (J-A+1)(J+A)u_3'' - (J-1)u_3'' - (J) + (J+A-2)(J+A+1)u_3'' + (J-1) \times$ $\times u_3'' + (J) + 8(J-A-1)(J-A+1)(J+A+1)(J+A+1)^2 \}^2$
${}^Q_3(J)$	${}^Q_3(J)$	$\frac{(J-A)(J+A+1)(2J+1)}{32J(J+1)C_3''(J)C_3''(J)} \{ (J-A+1)(J+A)u_3'' - (J)u_3'' - (J) + (J-A-1)(J+A+2) \times$ $\times u_3'' + (J)u_3'' + (J) + 8(J-A)(J-A+1)(J+A+1)(J+A+1)(J+A+2) \}^2$
${}^R_3(J)$	${}^P_3(J+1)$	$\frac{(J+A+1)(J+A+2)}{32(J+1)C_3''(J+1)C_3''(J)} \{ (J-A+1)(J+A)u_3'' - (J+1)u_3'' - (J) + (J-A)(J+A+3)u_3'' + (J+1) \times$ $\times u_3'' + (J) + 8(J-A+1)^2(J+A+1)(J+A+3) \}^2$

$$C_1(J) = A^2(Y-2)^2(J-A+1)(J+A); \quad C_2(J) = A^2(Y-2)^2$$

$$C_3(J) = A^2(Y-2)^2(J-A)(J+A+1) \quad (1)$$

and in the case of an inverted term ($Y < 0$) the signs are to be interchanged in the first row, and in the second row $-A$ is to be written, instead of $+A$; furthermore, $|Y| = \infty$. For case *b* terms, the required substitutions are

$$u_1^+(J) = 2(J-A); \quad u_1^-(J) = 2(J+A); \quad u_3^+(J) = 2(J-A+1)$$

$$u_3^-(J) = 2(J+A+1) \quad (2)$$

$$C_1(J) = 2(2J+1)(J-A)J(J+A); \quad C_2(J) = 4J(J+1)$$

$$C_3(J) = 2(2J+1)(J-A+1)(J+1)(J+A+1)$$

The above results hold for electric di-pole radiation. As regards ${}^3\Sigma$ terms, only the transitions ${}^3\Sigma^+ \rightarrow {}^3\Sigma^+$ or ${}^3\Sigma^- \rightarrow {}^3\Sigma^-$ are possible in electric di-pole radiation. Present [183] has shown, however, that the spin-orbit interaction can account for the otherwise 'forbidden' transition ${}^3\Sigma^+ \rightarrow {}^3\Sigma^+$. Rotational perturbation can also result in such a transition but then the line strengths of the branches $\Delta N = \pm 2$ (where the superfix is either *S* or *O*) are all zero. The line strengths of the transitions brought about by the spin-orbit interaction are listed in Table 3.9. Details of the calculation will be given in Section 3.3.

The line strengths for the general intermediate case of transitions of different type (i.e. for $\Delta A = \pm 1$) are listed in Table 3.10. The A 's occurring explicitly in the formulas mean once more the smaller of the two A 's involved in the transition. The abbreviated notation is the same as that in Table 3.8. The appropriate substitution of the formulas in the third column give the line strengths of the branches given in the first column, for the transitions ${}^3\Pi \rightarrow {}^3\Sigma$, ${}^3\Delta \rightarrow {}^3\Pi$, ${}^3\Phi \rightarrow {}^3\Delta$, . . . , and the corresponding values of the branches given in the second column for the transitions ${}^3\Sigma \rightarrow {}^3\Pi$, ${}^3\Pi \rightarrow {}^3\Delta$, ${}^3\Delta \rightarrow {}^3\Phi$, The formulas for the limiting cases can be derived from the above ones by the substitutions (1) and (2). Some of these formulas, and certain line strengths of intermediate-case transitions for given values of A have already been known earlier. Thus the line strengths of the transitions ${}^3\Pi(a) \rightarrow {}^3\Sigma(b)$ and ${}^3\Pi(b) \rightarrow {}^3\Sigma(b)$ were given by Nolan and Jenkins [171], those of the transitions ${}^3\Pi(\text{int}) \rightarrow {}^3\Sigma(b)$ by Budó [21], and those of transitions ${}^3\Delta(a) \rightarrow {}^3\Pi(a)$, ${}^3\Delta(a) \rightarrow {}^3\Pi(\text{int})$, ${}^3\Delta(a) \rightarrow {}^3\Pi(b)$, ${}^3\Delta(\text{int}) \rightarrow {}^3\Pi(a)$, ${}^3\Delta(\text{int}) \rightarrow {}^3\Pi(b)$, ${}^3\Delta(b) \rightarrow {}^3\Pi(a)$, ${}^3\Delta(b) \rightarrow {}^3\Pi(\text{int})$, ${}^3\Delta(b) \rightarrow {}^3\Pi(b)$ by Kovács [110]; finally Kovács and Törös [129] gave the line strengths of the transitions ${}^3\Delta(\text{int}) \rightarrow {}^3\Pi(\text{int})$.

Among the above formulas, those of the transitions ${}^3\Pi(\text{int}) \rightarrow {}^3\Sigma(b)$ were applied by Budó [21] to the 0-0 bands of the PH molecule. The theoretical line strengths are compared in Fig. 3.5 with the observed one obtained from formula (3.1-23).

The formulas for the transition ${}^3\Delta(\text{int}) \rightarrow {}^3\Pi(\text{int})$ were applied by Kovács and Törös [129] to the 3-0 band of the $d\,{}^3\Delta \rightarrow a\,{}^3\Pi$ transition of the CO molecule. The theoretical line strengths are compared in Fig. 3.6 with the experimental values, obtained from (3.1-23), observed by Carroll [30].

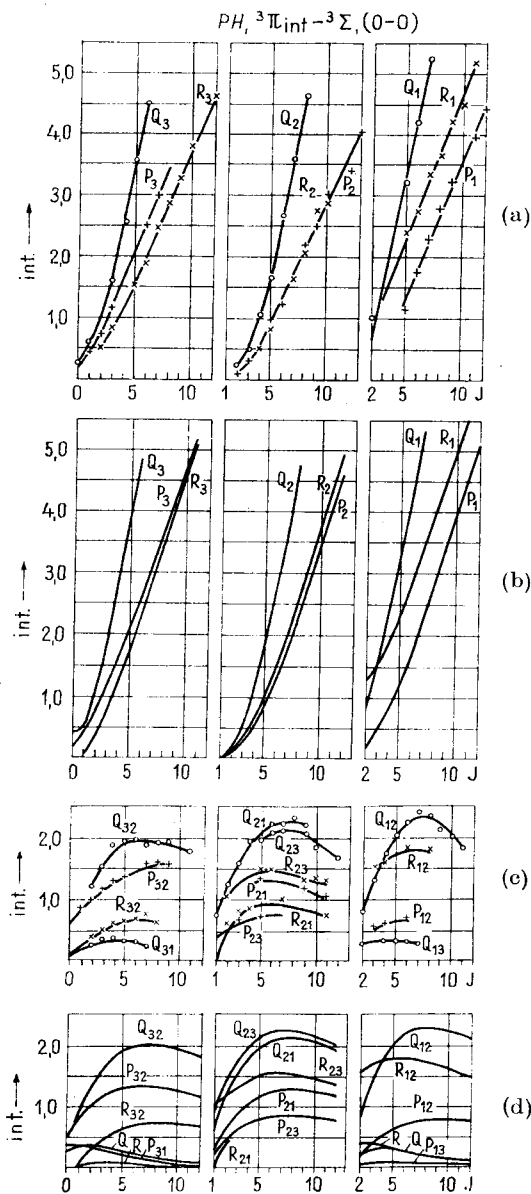


Fig. 3.5 Intensity distribution of the transitions ${}^3\Pi(\text{int}) - {}^3\Sigma$ of the PH molecule according to Budó [21], using formula (3.1-23). Curves in (a) and (c) represent the experimental findings, those in (b) and (d) show the theoretical results.

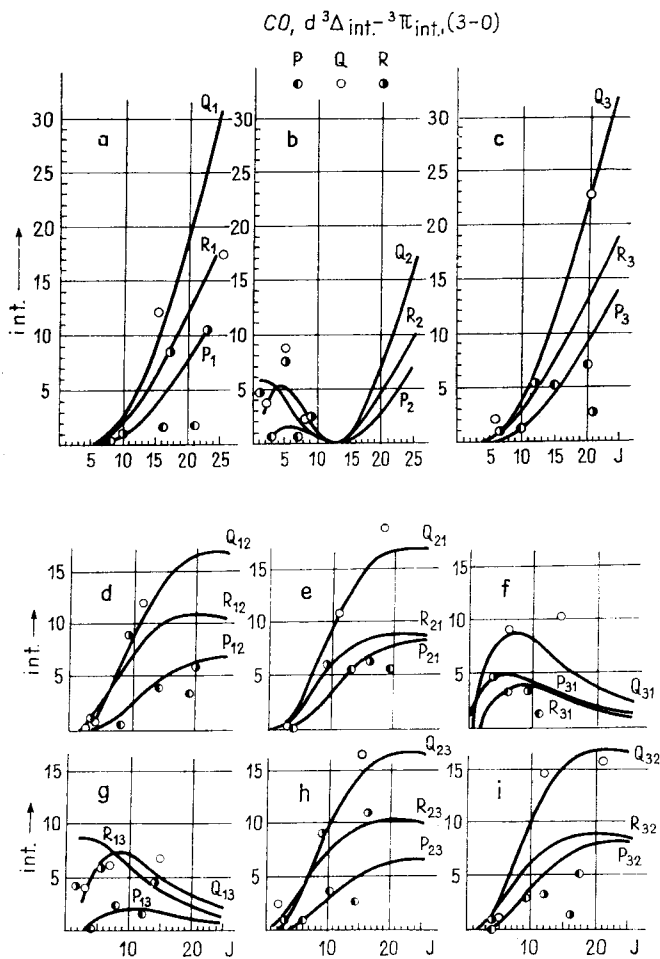


Fig. 3.6 Intensity distribution in the 3-0 band of the transition $d^3\Delta_{int} - ^3\Pi_{int}$ of the CO molecule, according to Kovács and Törös [129] using expression (3.1-23).

Owing to a spin-orbit interaction, the transitions corresponding to $\Delta J = \pm 2$ can also arise, although with intensities lower than those of transitions $\Delta J = 0, \pm 1$. The line strengths for the transitions $^3\Sigma - ^3\Sigma$, as given by Kovács [105], are listed in Table 3.11. For the notations used in the tables cf. (2.1.4-9) and (2.1.4-10), where now $J = 2$. The details of the calculation can be found in Section 3.3. By the substitutions (1) and (2) the limiting case formulas can be obtained from the above ones; they can also be found in ready form in [103].

Table 3.11. Line Strengths of Triplet Transition for $\Delta A = \pm 2$

Branches		Line strengths
$\Delta A = -2$	$\Delta A = +2$	${}^3\Sigma - {}^3A$ (int)
$P_1(J)$	$R_1(J-1)$	$\frac{(J+1)(J+2)}{2(2J-1)C_1(J)} \{(J-1)u_1^+(J) + 2(J-2)(J+2)\}^2$
$Q_1(J)$	$Q_1(J)$	$\frac{(J-1)(J+2)}{2JC_1(J)} \{Ju_1^+(J) + 2(J-2)(J+2)\}^2$
$R_1(J)$	$P_1(J+1)$	$\frac{(J-1)J(J+2)}{2(J+1)(2J+3)C_1(J)} \{(J+1)u_1^+(J) + 2(J-2)(J+2)\}^2$
${}^Q P_{21}(J)$	${}^Q R_{12}(J-1)$	$\frac{2(J-2)^2(J+1)(J+2)^3}{JC_1(J)}$
${}^R Q_{21}(J)$	${}^P Q_{12}(J)$	$\frac{2(J-2)^2(J-1)(J+2)^3(2J+1)}{J(J+1)C_1(J)}$
${}^S R_{21}(J)$	${}^O P_{12}(J+1)$	$\frac{2(J-2)^2(J-1)J(J+2)^2}{(J+1)C_1(J)}$
${}^R P_{31}(J)$	${}^P R_{13}(J-1)$	$\frac{(J-1)(J+1)(J+2)}{2J(2J-1)C_1(J)} \{Ju_1^+(J) - 2(J-2)(J+2)\}^2$
${}^S Q_{31}(J)$	${}^O Q_{13}(J)$	$\frac{(J-1)(J+2)}{2(J+1)C_1(J)} \{(J+1)u_1^+(J) - 2(J-2)(J+2)\}^2$
${}^T R_{31}(J)$	${}^N P_{13}(J+1)$	$\frac{(J-1)J(J+2)^2}{2(2J+3)C_1(J)} \{u_1^+(J) - 2(J-2)\}^2$
${}^O P_{12}(J)$	${}^S R_{21}(J-1)$	$\frac{4(J+1)(J+2)}{(2J-1)C_2(J)} \{Y - (J+1)\}^2$
${}^P Q_{12}(J)$	${}^R Q_{21}(J)$	$\frac{4(J-1)(J+2)}{JC_2(J)} \{Y - (J+2)\}^2$
${}^Q R_{12}(J)$	${}^Q P_{21}(J+1)$	$\frac{4(J-1)J(J+2)}{(J+1)(2J+3)C_2(J)} \{Y - (J+3)\}^2$
$P_2(J)$	$R_2(J-1)$	$\frac{4(J+1)(J+2)}{JC_2(J)} (Y-2)^2$
$Q_2(J)$	$Q_2(J)$	$\frac{4(J-1)(J+2)(2J+1)}{J(J+1)C_2(J)} (Y-2)^2$
$R_2(J)$	$P_2(J+1)$	$\frac{4(J-1)J}{(J+1)C_2(J)} (Y-2)^2$
${}^Q P_{32}(J)$	${}^Q R_{23}(J-1)$	$\frac{4(J-1)(J+1)(J+2)}{J(2J-1)C_2(J)} \{Y + (J-2)\}^2$
${}^R Q_{32}(J)$	${}^P Q_{23}(J)$	$\frac{4(J-1)(J+2)}{(J+1)C_2(J)} \{Y + (J-1)\}^2$
${}^S R_{32}(J)$	${}^O P_{23}(J+1)$	$\frac{4(J-1)J}{(2J+3)C_2(J)} \{Y + J\}^2$

Table 3.11 (*continued*)

Branches		Line strengths
$AA = -2$	$AA = +2$	${}^3\Sigma - {}^3A(\text{int})$
${}^N P_{13}(J)$	${}^T R_{31}(J-1)$	$\frac{(J-1)^2 (J+1) (J+2)}{2(2J-1)C_3(J)} \{u_3^-(J) - 2(J+3)\}^2$
${}^O Q_{13}(J)$	${}^S Q_{31}(J)$	$\frac{(J-1) (J+2)}{2JC_3(J)} \{Ju_3^-(J) - 2(J-1) (J+3)\}^2$
${}^P R_{13}(J)$	${}^R P_{31}(J+1)$	$\frac{(J-1)J(J+2)}{2(J+1) (2J+3)C_3(J)} \{(J+1)u_3^-(J) - 2(J-1) (J+3)\}^2$
${}^O P_{23}(J)$	${}^S R_{32}(J-1)$	$\frac{2(J-1)^2 (J+1) (J+2) (J+3)^2}{JC_3(J)}$
${}^P Q_{23}(J)$	${}^R Q_{32}(J)$	$\frac{2(J-1)^3 (J+2) (J+3)^2 (2J+1)}{J(J+1)C_3(J)}$
${}^Q R_{23}(J)$	${}^Q P_{32}(J+1)$	$\frac{2(J-1)^3 J(J+3)^2}{(J+1)C_3(J)}$
${}^P_3(J)$	${}^R_3(J-1)$	$\frac{(J-1) (J+1) (J+2)}{2J(2J-1)C_3(J)} \{Ju_3^-(J) + 2(J-1) (J+3)\}^2$
${}^Q_3(J)$	${}^Q_3(J)$	$\frac{(J-1) (J+2)}{2(J+1)C_3(J)} \{(J+1) u_3^-(J) + 2(J-1) (J+3)\}^2$
${}^R_3(J)$	${}^P_3(J+1)$	$\frac{(J-1)J}{2(2J+3)C_3(J)} \{(J+2) u_3^-(J) + 2(J-1) (J+3)\}^2$

3.2.4. *Quartet Transitions*

In the case of transitions of higher than triplet multiplicity, general formulas would be complicated. Since so far no 4A or ${}^4\Phi$ term is known whose rotational fine structure has been analysed, the transitions $A > 1$ do not, for the time being, have any practical importance. For this reason only the transitions of the Σ and Π terms will be considered when discussing transitions of higher multiplicity.

Even then, if the Π term corresponds to the intermediate case form, the application of (3.2-3) would entail lengthy calculations owing to the complexity of the transformation-matrix elements and for this reason the intermediate form has not yet been developed. We shall likewise restrict our treatment to the limiting-case transitions.

In the case of quartet transitions, the elements of the case *b* transformation matrix, necessary for the calculation by (3.2-3) of the line strengths for the case *b* transitions, can be obtained by appropriate substitutions from (2.1.5-6). However, in the quartet case as well as in the case of transitions of higher multiplicity, these elements can be directly obtained from (1.5-9), by substituting in it the case *b* energies from (2.1.1-5a) for the W_i 's

and putting $A = 0$ everywhere. The transformation-matrix elements calculated in this way for the terms ${}^4\Sigma$ and ${}^4\Pi$ are the following:

${}^4\Sigma(\mathbf{b})$ transformation matrix

$$\begin{aligned}
 S_{\mp 3/2, J-3/2} &= \pm \sqrt{\frac{J+3/2}{8J}}; & S_{\mp 1/2, J-3/2} &= \mp \sqrt{\frac{3(J-1/2)}{8J}} \\
 S_{\mp 3/2, J-1/2} &= -\sqrt{\frac{3(J+3/2)}{8(J+1)}}; & S_{\mp 1/2, J-1/2} &= +\sqrt{\frac{J-1/2}{8(J+1)}} \\
 S_{\mp 3/2, J+1/2} &= \pm \sqrt{\frac{3(J-1/2)}{8J}}; & S_{\mp 1/2, J+1/2} &= \pm \sqrt{\frac{J+3/2}{8J}} \\
 S_{\mp 3/2, J+3/2} &= -\sqrt{\frac{J-1/2}{8(J+1)}}; & S_{\mp 1/2, J+3/2} &= -\sqrt{\frac{3(J+3/2)}{8(J+1)}}
 \end{aligned} \tag{1}$$

${}^4\Pi(\mathbf{b})$ transformation matrix (Premaswarup [179])

$$\begin{aligned}
 S_{-1/2, J-3/2} &= +\sqrt{\frac{J-3/2}{8J}}; & S_{+1/2, J-3/2} &= -\sqrt{\frac{3(J-3/2)}{8J}} \\
 S_{+3/2, J-3/2} &= +\sqrt{\frac{3(J-3/2)(J+3/2)}{8J(J-1/2)}}; & S_{+5/2, J-3/2} &= -\sqrt{\frac{(J+3/2)(J+5/2)}{8J(J-1/2)}} \\
 S_{-1/2, J-1/2} &= -\sqrt{\frac{3(J+1/2)}{8(J+1)}}; & S_{+1/2, J-1/2} &= +\sqrt{\frac{(J+5/2)^2}{8(J+1)(J+1/2)}} \\
 S_{+3/2, J-1/2} &= +\sqrt{\frac{(J-7/2)^2(J+3/2)}{8(J+1)(J-1/2)(J+1/2)}} \\
 S_{+5/2, J-1/2} &= -\sqrt{\frac{3(J-3/2)(J+3/2)(J+5/2)}{8(J+1)(J-1/2)(J+1/2)}} \\
 S_{-1/2, J+1/2} &= +\sqrt{\frac{3(J+1/2)}{8J}}; & S_{+1/2, J+1/2} &= +\sqrt{\frac{(J-3/2)^2}{8J(J+1/2)}}
 \end{aligned} \tag{2}$$

$$S_{+3/2, J+1/2} = - \sqrt{\frac{(J - 1/2)(J + 9/2)^2}{8J(J + 1/2)(J + 3/2)}}$$

$$S_{+5/2, J+1/2} = - \sqrt{\frac{3(J - 3/2)(J - 1/2)(J + 5/2)}{8J(J + 1/2)(J + 3/2)}}$$

$$S_{-1/2, J+3/2} = - \sqrt{\frac{J + 5/2}{8(J + 1)}}; \quad S_{+1/2, J+3/2} = - \sqrt{\frac{3(J + 5/2)}{8(J + 1)}}$$

$$S_{+3/2, J+3/2} = - \sqrt{\frac{3(J - 1/2)(J + 5/2)}{8(J + 1)(J + 3/2)}}$$

$$S_{+5/2, J+3/2} = - \sqrt{\frac{(J - 3/2)(J - 1/2)}{8(J + 1)(J + 3/2)}}$$

By means of the case *a* amplitudes in Table 3.1 and of the above transformation matrices, the line strengths for limiting-case quartet transitions can be calculated by (3.2-3). Table 3.12 contains the line strengths of the ${}^4\Sigma \rightarrow {}^4\Sigma$ transitions according to Rao [187]; Table 3.13 lists the line strengths for the transitions ${}^4\Pi(a) \rightarrow {}^4\Pi(a)$, ${}^4\Pi(a) \rightarrow {}^4\Pi(b)$, ${}^4\Pi(b) \rightarrow {}^4\Pi(b)$ according to Premaswarup [179], and Table 3.14 lists the line strengths for the transitions ${}^4\Sigma \rightarrow {}^4\Pi(a)$, ${}^4\Sigma \rightarrow {}^4\Pi(b)$ as given by Budó [20].

Table 3.12. Line Strengths for ${}^4\Sigma \rightarrow {}^4\Sigma$ Transitions

Branches	Line strengths	Branches	Line strengths
	${}^4\Sigma \rightarrow {}^4\Sigma$		${}^4\Sigma \rightarrow {}^4\Sigma$
$P_1(J), R_1(J-1)$	$\frac{(2J-3)(2J+1)}{4(J-1)}$	${}^PQ_{12}(J), {}^RQ_{21}(J)$	$\frac{3(2J+1)}{4J^2}$
$P_2(J), R_2(J-1)$	$\frac{(J+1)(2J-3)(2J+1)}{4J}$	${}^PQ_{23}(J), {}^RQ_{32}(J)$	$\frac{(2J-1)(2J+1)(2J+3)}{4J^2(J+1)^2}$
$P_3(J), R_3(J-1)$	$\frac{(J-1)(2J-1)(2J+3)}{4J}$	${}^PQ_{34}(J), {}^RQ_{43}(J)$	$\frac{3(2J+1)}{4(J+1)^2}$
$P_4(J), R_4(J-1)$	$\frac{(2J-1)(2J+3)}{4(J+1)}$	${}^PR_{13}(J-1), {}^RP_{31}(J)$	$\frac{3}{4(J-1)J^2}$
		${}^PR_{24}(J-1), {}^RP_{42}(J)$	$\frac{3}{4J^2(J+1)}$

Table 3.13. Line Strengths for ${}^4\Pi$ - ${}^4\Pi$ Transitions

Branches	Line strengths		
	${}^4\Pi(a) - {}^4\Pi(a)$	${}^4\Pi(a) - {}^4\Pi(b)$	${}^4\Pi(b) - {}^4\Pi(b)$
$P_1(J)$	$\frac{(2J-1)(2J+1)}{4J}$	$\frac{(2J-3)(2J-1)(2J+1)}{64J^2}$	$\frac{(2J-5)(2J-1)(2J+1)}{4(J-1)(2J-3)}$
$Q_1(J)$	$\frac{2J+1}{4J(J+1)}$	$\frac{(2J-3)(2J+1)}{64J^2(J+1)}$	$\frac{4(J+1)(2J+1)}{J(2J-1)}$
$R_1(J)$	$\frac{(2J+1)(2J+3)}{4(J+1)}$	$\frac{(2J-3)(2J+1)(2J+3)}{64J(J+1)}$	$\frac{(2J-3)(2J+1)(2J+3)}{4J(2J-1)}$
$P_2(J)$	$\frac{(2J-1)(2J+1)}{4J}$	$\frac{(2J-1)(2J+5)^2}{64J(J+1)}$	$\frac{(J+1)(2J-3)^2(2J+1)^2}{4J^2(2J-1)}$
$Q_2(J)$	$\frac{2J+1}{4J(J+1)}$	$\frac{(2J+5)^2}{64J(J+1)^2}$	$\frac{4(J-4)^2(2J^2+1)}{(J+1)(2J-1)^2(2J+1)^2}$
$R_2(J)$	$\frac{(2J+1)(2J+3)}{4(J+1)}$	$\frac{(2J+3)(2J+5)^2}{64(J+1)^2}$	$\frac{(J+2)(2J-1)^2(2J+3)^2}{4(J+1)^2(2J+1)^2}$
$P_3(J)$	$\frac{(2J-3)(2J+3)}{4J}$	$\frac{(2J-3)(2J-1)(2J+9)^2}{64J^2(2J+1)}$	$\frac{(J-1)(2J-1)^2(2J+3)^2}{4J^2(2J+1)^2}$
$Q_3(J)$	$\frac{9(2J+1)}{4J(J+1)}$	$\frac{9(2J-1)(2J+9)^2}{64J^2(J+1)(2J+3)}$	$\frac{4(2J^2+3J-3)^2}{J(J+1)(2J+1)(2J+3)^2}$
$R_3(J)$	$\frac{(2J-1)(2J+5)}{4(J+1)}$	$\frac{(2J-1)^2(2J+5)(2J+9)^2}{64J(J+1)(2J+1)(2J+3)}$	$\frac{J(2J+1)^2(2J+5)^2}{4(J+1)^2(2J+3)^2}$
$P_4(J)$	$\frac{(2J-5)(2J+5)}{4J}$	$\frac{(2J-5)(2J-3)(2J-1)(2J+5)}{64J(J+1)(2J+3)}$	$\frac{(2J-1)(2J+1)(2J+5)}{4(J+1)(2J+3)}$
$Q_4(J)$	$\frac{25(2J+1)}{4J(J+1)}$	$\frac{25(2J-3)(2J-1)(2J+1)}{64J(J+1)^2(2J+3)}$	$\frac{4J(2J+1)}{(J+1)(2J+3)}$
$R_4(J)$	$\frac{(2J-3)(2J+7)}{4(J+1)}$	$\frac{(2J-3)^2(2J-1)(2J+7)}{64(J+1)^2(2J+3)}$	$\frac{(2J+1)(2J+3)(2J+7)}{4(J+2)(2J+5)}$

In Tables 3.13 and 3.14 the ${}^4\Pi$ terms are normal, with $Y > 0$. In the case of inverted terms with $Y < 0$, wherever the ${}^4\Pi(a)$ term occurs, the suffix referring to the inverted term in the branch symbol has to be changed according to the pattern $1 \rightarrow 4$, $2 \rightarrow 3$, $3 \rightarrow 2$, $4 \rightarrow 1$; e.g. in the case of ${}^4\Pi(a)_{\text{inv}} - {}^4\Pi(a)_{\text{norm}}$, $P_1 (= P_{11})$ becomes P_{41} , in the case of ${}^4\Pi(a)_{\text{norm}} - {}^4\Pi(a)_{\text{inv}}$, $P_1 (= P_{11})$ becomes P_{14} , whereas in the case of ${}^4\Pi(a)_{\text{inv}} - {}^4\Pi(a)_{\text{inv}}$, $P_1 (= P_{11})$ becomes $P_4 (= P_{44})$. Similar substitutions are necessary in Table 3.14; Table 3.13 lists only the line strengths belonging to the transitions $\Delta J = \Delta N = 0, \pm 1$ i.e. to the main branches.

Of the above theoretical line strengths, those belonging to the ${}^4\Sigma - {}^4\Sigma$ transitions were applied by Rao [187] to the 0-0 band of the CbO molecule

Table 3.14. Line Strengths for $^4\Sigma - ^4\Pi$ Transitions

Branches		Line strengths	
$^4\Sigma - ^4\Pi$	$^4\Pi - ^4\Sigma$	$^4\Sigma - ^4\Pi(a)$	$^4\Sigma - ^4\Pi(b)$
$P_1(J)$	$R_1(J-1)$	$\frac{(2J-3)(2J-1)(2J+1)}{128(J-1)J}$	$\frac{(2J-1)(2J+1)}{8(J-1)}$
$Q_1(J)$	$Q_1(J)$	$\frac{(2J-1)(2J+1)(2J+3)^2}{128J^2(J+1)}$	$\frac{(J+1)(2J-3)(2J+1)}{2J(2J-1)}$
$R_1(J)$	$P_1(J+1)$	$\frac{(2J+3)(2J+5)^2}{128(J+1)^2}$	$\frac{(2J-3)(2J+3)}{8J}$
$Q_{P_{21}}(J)$	$Q_{R_{12}}(J-1)$	$\frac{3(2J-3)(2J-1)(2J+1)}{128J^2}$	$\frac{3(2J+1)}{2J(2J-1)}$
$R_{Q_{21}}(J)$	$P_{Q_{12}}(J)$	$\frac{3(2J-1)(2J+1)(2J+3)^2}{128J(J+1)^2}$	$\frac{3(2J-3)(2J+1)}{8J^2(2J-1)}$
$S_{R_{21}}(J)$	$O_{P_{12}}(J+1)$	$\frac{3(2J+3)(2J+5)^2}{128(J+1)(J+2)}$	0
$R_{P_{31}}(J)$	$P_{R_{13}}(J-1)$	$\frac{3(2J-3)^2(2J-1)}{128(J-1)J}$	$\frac{3(2J-3)}{8(J-1)J^2(2J-1)}$
$S_{Q_{31}}(J)$	$O_{Q_{13}}(J)$	$\frac{3(2J-1)^2(2J+1)(2J+3)}{128J^2(J+1)}$	0
$T_{R_{31}}(J)$	$N_{P_{13}}(J+1)$	$\frac{3(2J+1)(2J+3)(2J+5)}{128(J+1)^2}$	0
$S_{P_{41}}(J)$	$O_{R_{14}}(J-1)$	$\frac{(2J-3)^2(2J-1)}{128J^2}$	0
$T_{Q_{41}}(J)$	$N_{Q_{14}}(J)$	$\frac{(2J-1)^2(2J+1)(2J+3)}{128J(J+1)^2}$	0
$U_{R_{41}}(J)$	$M_{P_{14}}(J)$	$\frac{(2J+1)(2J+3)(2J+5)}{128(J+1)(J+2)}$	0
$O_{P_{12}}(J)$	$S_{R_{21}}(J-1)$	$\frac{3(2J-3)(2J-1)(2J+1)}{128(J-1)J}$	0
$P_{Q_{12}}(J)$	$R_{Q_{21}}(J)$	$\frac{3(2J-1)(2J+1)^2}{128J^2(J+1)}$	$\frac{3(2J+1)^2}{8J^2(2J-1)}$
$Q_{R_{12}}(J)$	$Q_{P_{21}}(J+1)$	$\frac{3(2J+1)^2(2J+3)}{128(J+1)^2}$	$\frac{3(2J+3)}{2(J+1)(2J+1)}$
$P_2(J)$	$R_2(J-1)$	$\frac{(2J-3)(2J-1)(2J+1)}{128J^2}$	$\frac{(J+1)(2J-3)(2J+1)^2}{8J^2(2J-1)}$
$Q_2(J)$	$Q_2(J)$	$\frac{(2J-1)(2J+1)^3}{128J(J+1)^2}$	$\frac{(2J^2+J-4)^2}{2J(J+1)(2J-1)}$

Table 3.14 (*continued*)

Branches		Line strengths	
$^4\Sigma - ^4\Pi$	$^4\Pi - ^4\Sigma$	$^4\Sigma - ^4\Pi(a)$	$^4\Sigma - ^4\Pi(b)$
$R_2(J)$	$P_2(J+1)$	$\frac{(2J+1)^2(2J+3)}{128(J+1)(J+2)}$	$\frac{(J+2)(2J-1)^2(2J+3)}{8(J+1)^2(2J+1)}$
$^Q P_{32}(J)$	$^Q R_{23}(J-1)$	$\frac{(2J-1)(2J+1)^2}{128(J-1)J}$	$\frac{8(J-1)(J+1)}{J(2J-1)(2J+1)}$
$^R Q_{32}(J)$	$^P Q_{23}(J)$	$\frac{(2J+1)^3(2J+3)}{128J^2(J+1)}$	$\frac{(2J-1)^2(2J+3)}{8J^2(J+1)^2}$
$^S R_{32}(J)$	$^O P_{23}(J+1)$	$\frac{(2J+1)(2J+3)(2J+5)}{128(J+1)^2}$	0
$^R P_{42}(J)$	$^P R_{24}(J-1)$	$\frac{3(2J-1)(2J+1)^2}{128J^2}$	$\frac{3(2J-1)}{8J^2(J+1)(2J+1)}$
$^S Q_{42}(J)$	$^O Q_{24}(J)$	$\frac{3(2J+1)^3(2J+3)}{128J(J+1)^2}$	0
$^T R_{42}(J)$	$^N P_{24}(J+1)$	$\frac{3(2J+1)(2J+3)(2J+5)}{128(J+1)(J+2)}$	0
$^N P_{13}(J)$	$^T R_{31}(J-1)$	$\frac{3(2J-3)(2J+1)(2J+3)}{128(J-1)J}$	0
$^O Q_{13}(J)$	$^S Q_{31}(J)$	$\frac{3(2J-1)^2(2J+1)(2J+3)}{128J^2(J+1)}$	0
$^P R_{13}(J)$	$^R P_{31}(J+1)$	$\frac{3(2J-1)(2J+1)^2}{128(J+1)^2}$	$\frac{3(2J+3)}{8J(J+1)^2(2J+1)}$
$^O P_{23}(J)$	$^S R_{32}(J-1)$	$\frac{(2J-3)(2J+1)(2J+3)}{128J^2}$	0
$^P Q_{23}(J)$	$^R Q_{32}(J)$	$\frac{(2J-1)^2(2J+1)(2J+3)}{128J(J+1)^2}$	$\frac{(2J-1)(2J+3)^2}{8J^2(J+1)^2}$
$^Q R_{23}(J)$	$^Q P_{32}(J+1)$	$\frac{(2J-1)(2J+1)^2}{128(J+1)(J+2)}$	$\frac{8J(J+2)}{(J+1)(2J+1)(2J+3)}$
$P_3(J)$	$R_3(J-1)$	$\frac{(2J+1)^2(2J+3)}{128(J-1)J}$	$\frac{(J-1)(2J-1)(2J+3)^2}{8J^2(2J+1)}$
$Q_3(J)$	$Q_3(J)$	$\frac{(2J-1)(2J+1)(2J+3)^2}{128J^2(J+1)}$	$\frac{(2J^2+3J-3)^2}{2J(J+1)(2J+3)}$
$R_3(J)$	$P_3(J+1)$	$\frac{(2J-1)(2J+1)(2J+5)}{128(J+1)^2}$	$\frac{J(2J+1)^2(2J+5)}{8(J+1)^2(2J+3)}$
$^Q P_{43}(J)$	$^Q R_{34}(J-1)$	$\frac{3(2J+1)^2(2J+3)}{128J^2}$	$\frac{3(2J-1)}{2J(2J+1)}$

Table 3.14 (continued)

Branches		Line strengths	
$^4\Sigma - ^4\Pi$	$^4\Pi - ^4\Sigma$	$^4\Sigma - ^4\Pi(a)$	$^4\Sigma - ^4\Pi(b)$
$^RQ_{43}(J)$	$^PQ_{34}(J)$	$\frac{3(2J-1)(2J+1)(2J+3)^2}{128J(J+1)^2}$	$\frac{3(2J+1)^2}{8(J+1)^2(2J+3)}$
$^SR_{43}(J)$	$^OP_{34}(J+1)$	$\frac{3(2J-1)(2J+1)(2J+5)}{128(J+1)(J+2)}$	0
$^MP_{14}(J)$	$^UR_{41}(J-1)$	$\frac{(2J+1)(2J+3)(2J+5)}{128(J-1)J}$	0
$^NQ_{14}(J)$	$^TQ_{41}(J)$	$\frac{(2J-3)(2J+1)(2J+3)(2J+5)}{128J^2(J+1)}$	0
$^OR_{14}(J)$	$^SP_{41}(J+1)$	$\frac{(2J-3)(2J-1)(2J+5)}{128(J+1)^2}$	0
$^NP_{24}(J)$	$^TR_{42}(J-1)$	$\frac{3(2J+1)(2J+3)(2J+5)}{128J^2}$	0
$^OQ_{24}(J)$	$^SQ_{42}(J)$	$\frac{3(2J-3)(2J+1)(2J+3)(2J+5)}{128J(J+1)^2}$	0
$^PR_{24}(J)$	$^RP_{42}(J+1)$	$\frac{3(2J-3)(2J-1)(2J+5)}{128(J+1)(J+2)}$	$\frac{3(2J+5)}{8(J+1)^2(J+2)(2J+3)}$
$^OP_{34}(J)$	$^SR_{43}(J-1)$	$\frac{3(2J-3)(2J+3)(2J+5)}{128(J-1)J}$	0
$^PQ_{34}(J)$	$^RQ_{43}(J)$	$\frac{3(2J-3)(2J-1)(2J+1)(2J+5)}{128J^2(J+1)}$	$\frac{3(2J+1)(2J+5)}{8(J+1)^2(2J+3)}$
$^QR_{34}(J)$	$^QP_{43}(J+1)$	$\frac{3(2J-3)(2J-1)(2J+1)}{128(J+1)^2}$	$\frac{3(2J+1)}{2(J+1)(2J+3)}$
$P_4(J)$	$R_4(J-1)$	$\frac{(2J-3)(2J+3)(2J+5)}{128J^2}$	$\frac{(2J-1)(2J+5)}{8(J+1)}$
$Q_4(J)$	$Q_4(J)$	$\frac{(2J-3)(2J-1)(2J+1)(2J+5)}{128J(J+1)^2}$	$\frac{J(2J+1)(2J+5)}{2(J+1)(2J+3)}$
$R_4(J)$	$P_4(J+1)$	$\frac{(2J-3)(2J-1)(2J+1)}{128(J+1)(J+2)}$	$\frac{(2J+1)(2J+3)}{8(J+2)}$

(cf. Fig. 3.7). Rao used procedure (3.1-23), but without dividing by the Boltzmann factor.

Nevin [163] observed a $^4\Sigma-^4\Pi$ transition in the O_2^+ molecule and published estimated intensity values for some of the lines. These values have not, however, been confronted with the theoretical formulas. The agreement is liable to be rather moderate, since the $^4\Pi$ term in this case is definitely intermediate in the quantum number range observed.

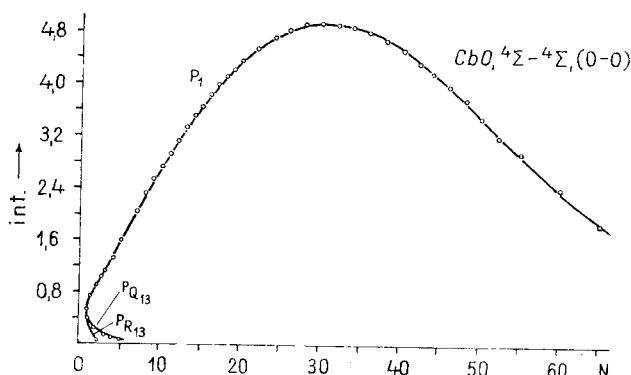


Fig. 3.7 Intensity distribution in the 0-0 band of the transition ${}^4\Sigma-{}^4\Sigma$ of the CbO molecule, according to Rao [187] using the formula (3.1-23); division by the Boltzmann factor has not been applied; only the intensities of the branches P_1 , $P_{Q_{13}}$ and $P_{R_{13}}$ are given.

3.2.5. Quintet Transitions

For quintet transitions—as in the quartet transitions—again only the line strengths belonging to the limiting-case transitions with respect to the Σ and Π terms are known. The transformation-matrix elements, required in addition to the case a amplitudes (Table 3.1), if (3.2-3) is to be used, have not been published in the literature; they can be calculated in the same manner as indicated above. The transformation-matrix elements for the ${}^5\Sigma$ terms are given below.

$$S_{\mp 2, J-2} = + \sqrt{\frac{(J+1)(J+2)}{4(2J-1)(2J+1)}}; \quad S_{\mp 1, J-2} = - \sqrt{\frac{(J-1)(J+1)}{(2J-1)(2J+1)}}$$

$$S_{0, J-2} = + \sqrt{\frac{3J(J-1)}{2(2J-1)(2J+1)}}$$

$$S_{\mp 2, J-1} = \pm \sqrt{\frac{J+2}{2(2J+1)}}; \quad S_{\mp 1, J-1} = \mp \sqrt{\frac{J-1}{2(2J+1)}}; \quad S_{0, J-1} = 0$$

$$S_{\mp 2, J} = + \sqrt{\frac{3(J-1)(J+2)}{2(2J-1)(2J+3)}}; \quad S_{\mp 1, J} = + \sqrt{\frac{3}{2(2J-1)(2J+3)}}$$

$$S_{0, J} = - \sqrt{\frac{J(J+1)}{(2J-1)(2J+3)}}$$

$$\begin{aligned}
 S_{\pm 2, J+1} &= \pm \sqrt{\frac{J-1}{2(2J+1)}}; \quad S_{\pm 1, J+1} = \pm \sqrt{\frac{J+2}{2(2J+1)}}; \quad S_{0, J+1} = 0 \\
 S_{\pm 2, J+2} &= + \sqrt{\frac{(J-1)J}{4(2J+1)(2J+3)}}; \quad S_{\pm 1, J+2} = + \sqrt{\frac{J(J+2)}{(2J+1)(2J+3)}} \\
 S_{0, J+2} &= + \sqrt{\frac{3(J+1)(J+2)}{2(2J+1)(2J+3)}} \quad (1)
 \end{aligned}$$

Table 3.15 lists the line strengths for the transition ${}^5\Sigma \rightarrow {}^5\Sigma$, Table 3.16 for ${}^5\Pi(a) \rightarrow {}^5\Pi(a)$, ${}^5\Pi(a) \rightarrow {}^5\Pi(b)$, ${}^5\Pi(b) \rightarrow {}^5\Pi(b)$, and Table 3.17 for ${}^5\Sigma \rightarrow {}^5\Pi(a)$, ${}^5\Sigma \rightarrow {}^5\Pi(b)$ all as derived by Premaswarup [178, 179] from the above formulas.

Table 3.15. Line Strengths for ${}^5\Sigma \rightarrow {}^5\Sigma$ Transitions

Branches	Line strengths	Branches	Line strengths
	${}^5\Sigma \rightarrow {}^5\Sigma$		${}^5\Sigma \rightarrow {}^5\Sigma$
$P_1(J), R_1(J-1)$	$\frac{(J-2)(2J+1)}{2J-3}$	${}^PQ_{23}(J)$	$\frac{3(J-1)(2J+3)}{J(J+1)(2J-1)}$
$P_2(J), R_2(J-1)$	$\frac{(J-2)(J+1)(2J+1)}{J(2J-1)}$	${}^RQ_{32}(J)$	$\frac{J(J+1)(2J-1)}{J(J+1)(2J+3)}$
$P_3(J), R_3(J-1)$	$\frac{(J-1)(J+1)(2J-3)(2J+3)}{J(2J-1)(2J+1)}$	${}^PQ_{34}(J)$	$\frac{3(J+2)(2J-1)}{J(J+1)(2J+3)}$
$P_4(J), R_4(J-1)$	$\frac{(J-1)(J+2)(2J-1)}{J(2J+1)}$	${}^RQ_{43}(J)$	$\frac{2(2J+1)}{(J+1)(2J+3)}$
$P_5(J), R_5(J-1)$	$\frac{(J+2)(2J-1)}{2J+3}$	${}^PQ_{45}(J)$	$\frac{6}{J(2J-3)(2J-1)}$
${}^PQ_{12}(J), {}^RQ_{21}(J)$	$\frac{2(2J+1)}{J(2J-1)}$	${}^RQ_{54}(J)$	$\frac{9}{J(2J-1)(2J+1)}$
		${}^PR_{13}(J-1)$	$\frac{6}{J(2J+1)(2J+3)}$
		${}^RP_{31}(J)$	
		${}^PR_{24}(J-1)$	
		${}^RP_{42}(J)$	
		${}^PR_{35}(J-1)$	
		${}^RP_{53}(J)$	

In Tables 3.16 and 3.17, the ${}^5\Pi$ terms are assumed to be normal. In the case of inverted terms, wherever the ${}^5\Pi(a)$ term occurs, the suffix referring to it in the branch symbol has to be changed according to the pattern $1 \rightarrow 5$, $2 \rightarrow 4$, etc. Table 3.16 lists only the branches arising from the transitions $\Delta J = \Delta N = 0, \pm 1$, Table 3.17 only those arising from $\Delta J = 0, \pm 1$ and $\Delta N = 0, \pm 1$, of the possible 75 branches. The case b line strengths of the unlisted branches are either identically zero or converge fast to zero with increasing rotational quantum number.

The theoretical line strengths of quintet terms have not so far been verified experimentally.

Table 3.16. Line Strengths for ${}^5\Pi - {}^5\Pi$ Transitions

Branches	Line strengths		
	${}^5\Pi(a) - {}^5\Pi(a)$	${}^5\Pi(a) - {}^5\Pi(b)$	${}^5\Pi(b) - {}^5\Pi(b)$
$P_1(J)$	$\frac{(J-1)(J+1)}{J}$	$\frac{(J-2)(J-1)(J+1)^2}{4(2J-1)(2J+1)}$	$\frac{(J-3)(J-1)(2J+1)}{(J-2)(2J-3)}$
$Q_1(J)$	$\frac{2J+1}{J(J+1)}$	$\frac{J-2}{4J(2J-1)}$	$\frac{(J+1)(2J+1)}{(J-1)^2J}$
$R_1(J)$	$\frac{J(J+2)}{J+1}$	$\frac{(J-2)J(J+2)}{4(2J-1)(2J+1)}$	$\frac{(J-2)J(2J+3)}{(J-1)(2J-1)}$
$P_2(J)$	J	$\frac{J(J+1)}{2(2J+1)}$	$\frac{(J-2)^2(J+1)(2J+1)}{(J-1)^2(2J-1)}$
$Q_2(J)$	0	0	$\frac{(J^2-3)^2(2J+1)}{(J-1)^2J^3(J+1)}$
$R_2(J)$	$J+1$	$\frac{(J+1)^2}{2(2J+1)}$	$\frac{(J-1)^2(J+2)(2J+3)}{J^2(2J+1)}$
$P_3(J)$	$\frac{(J-1)(J+1)}{J}$	$\frac{(J-1)(J^2+J-3)^2}{J^2(2J-1)(2J+3)}$	$\frac{(J-1)^2(J+1)^2(2J-3)(2J+3)}{J^3(2J-1)(2J+1)}$
$Q_3(J)$	$\frac{2J+1}{J(J+1)}$	$\frac{(J^2+J-3)^2(2J+1)}{J^2(J+1)^2(2J-1)(2J+3)}$	$\frac{(J^2+J-3)^2(2J+1)}{J^3(J+1)^3}$
$R_3(J)$	$\frac{J(J+2)}{J+1}$	$\frac{(J+2)(J^2+J-3)^2}{(J+1)^2(2J-1)(2J+3)}$	$\frac{J^2(J+2)^2(2J-1)(2J+5)}{(J+1)^3(2J+1)(2J+3)}$
$P_4(J)$	$\frac{(J-2)(J+2)}{J}$	$\frac{(J-2)(J-1)(J+4)^2}{2J(J+1)(2J+1)}$	$\frac{(J-1)(J+2)^2(2J-1)}{(J+1)^2(2J+1)}$
$Q_4(J)$	$\frac{4(2J+1)}{J(J+1)}$	$\frac{2(J-1)(J+4)^2}{J(J+1)^2(J+2)}$	$\frac{(J^2+2J-2)^2(2J+1)}{J(J+1)^3(J+2)^2}$
$R_4(J)$	$\frac{(J-1)(J+3)}{J+1}$	$\frac{(J-1)^2(J+3)(J+4)^2}{2(J+1)^2(J+2)(2J+1)}$	$\frac{J(J+3)^2(2J+1)}{(J+2)^2(2J+3)}$
$P_5(J)$	$\frac{(J-3)(J+3)}{J}$	$\frac{(J-3)(J-2)(J-1)(J+3)}{4(J+2)(2J+1)(2J+3)}$	$\frac{(J+1)(J+3)(2J-1)}{(J+2)(2J+3)}$
$Q_5(J)$	$\frac{9(2J+1)}{J(J+1)}$	$\frac{9(J-2)(J-1)}{4(J+1)(J+2)(2J+3)}$	$\frac{J(2J+1)}{(J+1)(J+2)^2}$
$R_5(J)$	$\frac{(J-2)(J+4)}{J+1}$	$\frac{(J-2)^2(J-1)J(J+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$	$\frac{(J+2)(J+4)(2J+1)}{(J+3)(2J+5)}$

Table 3.17. Line Strengths for ${}^5\Pi - {}^5\Sigma$ Transitions

Branches		Line strengths	
${}^5\Pi - {}^5\Sigma$	${}^5\Sigma - {}^5\Pi$	${}^5\Pi(a) - {}^5\Sigma$	${}^5\Pi(b) - {}^5\Sigma$
$P_1(J)$	$R_1(J-1)$	$\frac{(J+1)^2 (J+2)^2}{8J(2J-1)(2J+1)}$	$\frac{(J-3)(2J+1)}{2(2J-3)}$
$Q_1(J)$	$Q_1(J)$	$\frac{(J-1)(J+2)^2}{8J(2J-1)}$	$\frac{(J-2)(J+1)(2J+1)}{2(J-1)J}$
$R_1(J)$	$P_1(J+1)$	$\frac{(J-1)J(J+2)}{8(2J-1)(2J+1)}$	$\frac{J(2J+3)}{2(2J-1)}$
${}^Q P_{21}(J)$	${}^Q R_{12}(J-1)$	$\frac{(J-1)(J+1)^2}{2(2J-1)(2J+1)}$	$\frac{2J+1}{(J-1)J}$
${}^R Q_{21}(J)$	${}^P Q_{12}(J)$	$\frac{(J-1)(J+1)}{2(2J-1)}$	$\frac{2J+1}{(J-1)(2J-1)}$
${}^P Q_{12}(J)$	${}^R Q_{21}(J)$	$\frac{(J-1)(J+2)^2 (J+3)^2 (2J+1)}{4J(J+1)(J^2+2J+3)(5J+3)}$	$\frac{(J-2)(2J+1)}{(J-1)J(2J-1)}$
${}^Q R_{12}(J)$	${}^Q P_{21}(J+1)$	$\frac{(J-1)J(J+2)(J+3)^2}{4(J+1)(J^2+2J+3)(5J+3)}$	$\frac{2J+3}{J(J+1)}$
$P_2(J)$	$R_2(J-1)$	$\frac{(J-1)(J+1)(J+3)^2}{4(J^2+2J+3)(5J+3)}$	$\frac{(J-2)^2 (J+1)(2J+1)}{2(J-1)J(2J-1)}$
$Q_2(J)$	$Q_2(J)$	$\frac{(J-1)(J+3)^2 (2J+1)}{4(J^2+2J+3)(5J+3)}$	$\frac{(J^2-3)^2 (2J+1)}{2(J-1)J^2(J+1)}$
$R_2(J)$	$P_2(J+1)$	$\frac{(J-1)J(J+3)^2}{4(J^2+2J+3)(5J+3)}$	$\frac{(J-1)(J+2)(2J+3)}{2J(2J+1)}$
${}^Q P_{32}(J)$	${}^Q R_{23}(J-1)$	$\frac{3(J-1)^2 J(J+1)}{2(J^2+2J+3)(5J+3)}$	$\frac{3(J+1)(2J-3)}{2(J-1)J^2}$
${}^R Q_{32}(J)$	${}^P Q_{23}(J)$	$\frac{3(J-1)J(J+1)(2J+1)}{2(J^2+2J+3)(5J+3)}$	$\frac{3(J-1)(2J+3)}{2J^2(2J-1)}$
${}^P Q_{23}(J)$	${}^R Q_{32}(J)$	$\frac{3(2J+1)}{4(2J-1)(2J+3)}$	$\frac{3(J-1)^2 (2J+3)}{2J^2 (J+1)(2J-1)}$
${}^Q R_{23}(J)$	${}^Q P_{32}(J+1)$	$\frac{3J}{4(2J-1)(2J+3)}$	$\frac{3(J+2)(2J-1)}{2J(J+1)^2}$
$P_3(J)$	$R_3(J-1)$	$\frac{(J-1)J(J+1)}{2(2J-1)(2J+3)}$	$\frac{(J-1)^2 (J+1)(2J-3)(2J+3)}{2J^2(2J-1)(2J+1)}$
$Q_3(J)$	$Q_3(J)$	$\frac{J(J+1)(2J+1)}{2(2J-1)(2J+3)}$	$\frac{(J^2+J-3)(2J+1)}{2J^2(J+1)^2}$
$R_3(J)$	$P_3(J+1)$	$\frac{J(J+1)(J+2)}{2(2J-1)(2J+3)}$	$\frac{J(J+2)^2 (2J-1)(2J+5)}{2(J+1)^2 (2J+1)(2J+3)}$

Table 3.17 (*continued*)

Branches		Line strengths	
${}^5\Pi-{}^5\Sigma$	${}^5\Sigma-{}^5\Pi$	${}^5\Pi(a)-{}^5\Sigma$	${}^5\Pi(b)-{}^5\Sigma$
${}^Q P_{43}(J)$	${}^Q R_{34}(J-1)$	$\frac{3(J-2)(J-1)}{4J(2J-1)(2J+3)}$	$\frac{3(J-1)(2J+3)}{2J^2(J+1)}$
${}^R Q_{43}(J)$	${}^P Q_{34}(J)$	$\frac{3(J-1)(J+2)(2J+1)}{4J(J+1)(2J-1)(2J+3)}$	$\frac{3(J+2)^2(2J-1)}{2J(J+1)^2(2J+3)}$
${}^P Q_{34}(J)$	${}^R Q_{43}(J)$	$\frac{3J(J+1)(J+2)(2J+1)}{2(J^2+2)(5J+2)}$	$\frac{3(J+2)(2J-1)}{2(J+1)^2(2J+3)}$
${}^Q R_{34}(J)$	${}^Q P_{43}(J+1)$	$\frac{3J(J+1)(J+2)^2}{2(J^2+2)(5J+2)}$	$\frac{3J(2J+5)}{2(J+1)^2(J+2)}$
$P_4(J)$	$R_4(J-1)$	$\frac{(J-2)^3(J-1)(J+2)}{4J(J^2+2)(5J+2)}$	$\frac{(J-1)(J+2)(2J-1)}{2(J+1)(2J+1)}$
$Q_4(J)$	$Q_4(J)$	$\frac{(J-2)^2(J-1)(J+2)^2(2J+1)}{4J(J+1)(J^2+2)(5J+2)}$	$\frac{(J^2+2J-2)^2(2J+1)}{2J(J+1)^2(J+2)}$
$R_4(J)$	$P_4(J+1)$	$\frac{(J-2)^2(J+2)^2(J+3)}{4(J+1)(J^2+2)(5J+2)}$	$\frac{J(J+3)^2(2J+1)}{2(J+1)(J+2)(2J+3)}$
${}^Q P_{54}(J)$	${}^Q R_{45}(J-1)$	$\frac{(J-3)(J-2)^3(J-1)}{4J(J^2+2)(5J+2)}$	$\frac{2J-1}{J(J+1)}$
${}^R Q_{54}(J)$	${}^P Q_{45}(J)$	$\frac{(J-2)^3(J-1)(J+3)(2J+1)}{4J(J+1)(J^2+2)(5J+2)}$	$\frac{(J+3)(2J+1)}{(J+1)(J+2)(2J+3)}$
${}^P Q_{45}(J)$	${}^R Q_{54}(J)$	$\frac{(J-1)(J+2)^2}{2(J+1)(2J+3)}$	$\frac{2J+1}{(J+2)(2J+3)}$
${}^Q R_{45}(J)$	${}^Q P_{54}(J+1)$	$\frac{J(J+2)^2(J+3)}{2(J+1)(2J+1)(2J+3)}$	$\frac{2J+1}{(J+1)(J+2)}$
$P_5(J)$	$R_5(J-1)$	$\frac{(J-3)(J-2)(J-1)}{8(2J+1)(2J+3)}$	$\frac{(J+1)(2J-1)}{2(2J+3)}$
$Q_5(J)$	$Q_5(J)$	$\frac{(J-2)(J-1)(J+3)}{8(J+1)(2J+3)}$	$\frac{J(J+3)(2J+1)}{2(J+1)(J+2)}$
$R_5(J)$	$P_5(J+1)$	$\frac{(J-1)(J+3)(J+4)}{8(2J+1)(2J+3)}$	$\frac{(J+4)(2J+1)}{2(2J+5)}$

3.2.6. Sextet Transitions

As in the previous case, only the line strengths of limiting-case transitions connected with Σ and Π terms have been derived for sextet terms. Of the transformation-matrix elements, only those for ${}^6\Sigma$ terms will be given here.

According to Kovács and Scari [126], these are

$$S_{\mp 5/2, J-5/2} = \mp 1/4 \left| \sqrt{\frac{(J+3/2)(J+5/2)}{2(J-1)J}} \right|$$

$$S_{\mp 3/2, J-5/2} = \pm 1/4 \left| \sqrt{\frac{5(J-3/2)(J+3/2)}{2(J-1)J}} \right|$$

$$S_{\mp 1/2, J-5/2} = \mp 1/4 \left| \sqrt{\frac{5(J-3/2)(J-1/2)}{(J-1)J}} \right|$$

$$S_{\mp 5/2, J-3/2} = -1/4 \left| \sqrt{\frac{5(J+3/2)(J+5/2)}{2J(J+1)}} \right|$$

$$S_{\mp 3/2, J-3/2} = +3/4 \left| \sqrt{\frac{(J-3/2)(J+3/2)}{2J(J+1)}} \right|$$

$$S_{\mp 1/2, J-3/2} = -1/4 \left| \sqrt{\frac{(J-3/2)(J-1/2)}{J(J+1)}} \right|$$

$$S_{\mp 5/2, J-1/2} = \mp 1/4 \left| \sqrt{\frac{5(J-3/2)(J+5/2)}{(J-1)(J+1)}} \right|$$

$$S_{\mp 3/2, J-1/2} = \pm 1/4 \left| \sqrt{\frac{(J-7/2)^2}{(J-1)(J+1)}} \right|$$

$$S_{\mp 1/2, J-1/2} = \pm 1/4 \left| \sqrt{\frac{2(J-1/2)(J+3/2)}{(J-1)(J+1)}} \right|$$

$$S_{\mp 5/2, J+1/2} = -1/4 \left| \sqrt{\frac{5(J-3/2)(J+5/2)}{J(J+2)}} \right|$$

$$S_{\mp 3/2, J+1/2} = -1/4 \left| \sqrt{\frac{(J+9/2)^2}{J(J+2)}} \right|$$

(continued) (1)

(1) (continued)

$$\begin{aligned}
 S_{\mp 1/2, J+1/2} &= + \frac{1}{4} \sqrt{\frac{2(J - 1/2)(J + 3/2)}{J(J + 2)}} \\
 S_{\mp 5/2, J+3/2} &= \mp \frac{1}{4} \sqrt{\frac{5(J - 1/2)(J - 3/2)}{2J(J + 1)}} \\
 S_{\mp 3/2, J+3/2} &= \mp \frac{3}{4} \sqrt{\frac{(J - 1/2)(J + 5/2)}{2J(J + 1)}} \\
 S_{\mp 1/2, J+3/2} &= \mp \frac{1}{4} \sqrt{\frac{(J + 3/2)(J + 5/2)}{J(J + 1)}} \\
 S_{\mp 5/2, J+5/2} &= - \frac{1}{4} \sqrt{\frac{(J - 1/2)(J - 3/2)}{2(J + 1)(J + 2)}} \\
 S_{\mp 3/2, J+5/2} &= - \frac{1}{4} \sqrt{\frac{5(J - 1/2)(J + 5/2)}{2(J + 1)(J + 2)}} \\
 S_{\mp 1/2, J+5/2} &= - \frac{1}{4} \sqrt{\frac{5(J + 3/2)(J + 5/2)}{(J + 1)(J + 2)}}
 \end{aligned} \tag{1}$$

The above formulas and the transformation-matrix elements for the ${}^6\Pi$ term derived in a similar manner from (1.5-9), were used following Premaswarup [178, 180] to calculate by Table 3.1 and (3.2-3) the line strengths listed in Table 3.18 for the transitions ${}^6\Sigma \rightarrow {}^6\Sigma$, in Table 3.19 for ${}^6\Pi(a) \rightarrow {}^6\Pi(a)$, ${}^6\Pi(a) \rightarrow {}^6\Pi(b)$ and ${}^6\Pi(b) \rightarrow {}^6\Pi(b)$, and in Table 3.20 for ${}^6\Sigma \rightarrow {}^6\Pi(a)$ and ${}^6\Sigma \rightarrow {}^6\Pi(b)$.

Wherever in Tables 3.19 and 3.20 an inverted ${}^6\Pi(a)$ term occurs, one has to change, as in the previous cases, the suffix referring to the inverted term in the branch symbol according to the pattern $1 \rightarrow 6$, $2 \rightarrow 5$, etc. Of the possible 108 branches, Tables 3.19 and 3.20 list first of all the main branches arising from the transitions $\Delta J = \Delta N = 0, \pm 1$; furthermore, for branches with $\Delta N \neq 0, \pm 1$, the line strengths of one characteristic branch are given for each ΔN .

Table 3.18. Line Strengths for ${}^6\Sigma-{}^6\Sigma$ Transitions

Branches		Line strengths
		${}^6\Sigma-{}^6\Sigma$
$P_1(J),$	$R_1(J-1)$	$\frac{(2J-5)(2J+1)}{4(J-2)}$
$P_2(J),$	$R_2(J-1)$	$\frac{(J+1)(2J-5)(2J+1)}{4(J-1)J}$
$P_3(J),$	$R_3(J-1)$	$\frac{(J-2)(J+1)(2J-3)(2J+3)}{4(J-1)J^2}$
$P_4(J),$	$R_4(J-1)$	$\frac{(J-1)(J+2)(2J-3)(2J+3)}{4J^2(J+1)}$
$P_5(J),$	$R_5(J-1)$	$\frac{(J-1)(2J-1)(2J+5)}{4J(J+1)}$
$P_6(J),$	$R_6(J-1)$	$\frac{(2J-1)(2J+5)}{4(J+2)}$
$PQ_{12}(J),$	$RQ_{21}(J)$	$\frac{5(2J-1)}{4J(J+1)}$
$PQ_{23}(J),$	$RQ_{32}(J)$	$\frac{(2J-3)(2J+1)(2J+3)}{2(J-1)J^2(J+1)}$
$PQ_{34}(J),$	$RQ_{43}(J)$	$\frac{9(J-1)(J+2)(2J+1)}{4J^2(J+1)^2}$
$PQ_{45}(J),$	$RQ_{54}(J)$	$\frac{(2J-1)(2J+1)(2J+5)}{2J(J+1)^2(J+2)}$
$PQ_{56}(J),$	$RQ_{65}(J)$	$\frac{5(2J+1)}{4(J+1)(J+2)}$
$P_{R_{13}}(J-1),$	$R_{P_{31}}(J)$	$\frac{5}{2(J-2)(J-1)J}$
$P_{R_{24}}(J-1),$	$R_{P_{42}}(J)$	$\frac{9}{2(J-1)J^2}$
$P_{R_{35}}(J-1),$	$R_{P_{53}}(J)$	$\frac{9}{2J^2(J+1)}$
$P_{R_{46}}(J-1),$	$R_{P_{64}}(J)$	$\frac{5}{2J(J+1)(J+2)}$

Table 3.19. Line Strengths for ${}^6\Pi-{}^6\Pi$ Transitions

Branches	Line strengths		
	${}^6\Pi(a)-{}^6\Pi(a)$	${}^6\Pi(a)-{}^6\Pi(b)$	${}^6\Pi(b)-{}^6\Pi(b)$
$P_1(J)$	$\frac{(2J-3)(2J+3)}{4J}$	$\frac{(2J-5)(2J-3)(2J+3)^2}{512(J-1)J^2}$	$\frac{(2J-7)(2J-3)(2J+1)}{4(J-2)(2J-5)}$
$Q_1(J)$	$\frac{9(2J+1)}{4J(J+1)}$	$\frac{9(2J-5)(2J+1)(2J+3)}{512(J-1)J^2(J+1)}$	$\frac{4(J+1)(2J+1)}{J(2J-3)^2}$
$R_1(J)$	$\frac{(2J-1)(2J+5)}{4(J+1)}$	$\frac{(2J-5)(2J-1)(2J+3)(2J+5)}{512(J-1)J(J+1)}$	$\frac{(2J-5)(2J-1)(2J+3)}{4(J-1)(2J-3)}$
$P_2(J)$	$\frac{(2J-1)(2J+1)}{4J}$	$\frac{(2J-1)(2J+1)(6J+1)^2}{512J^2(J+1)}$	$\frac{(J+1)(2J-5)^2(2J-1)(2J+1)}{(J-1)J(2J-3)^2}$
$Q_2(J)$	$\frac{2J+1}{4J(J+1)}$	$\frac{(2J+1)(6J+1)^2}{512J^2(J+1)^2}$	$\frac{4(2J+1)(2J^2-J-8)^2}{J(J+1)(2J-3)^2(2J-1)^2}$
$R_2(J)$	$\frac{(2J+1)(2J+3)}{4(J+1)}$	$\frac{(2J+1)(2J+3)(6J+1)^2}{512J(J+1)^2}$	$\frac{(J+2)(2J-3)^2(2J+1)(2J+3)}{4J(J+1)(2J-1)^2}$
$P_3(J)$	$\frac{(2J-1)(2J+1)}{4J}$	$\frac{(2J-5)^2(2J-1)(2J+3)}{128(J-1)J(J+1)}$	$\frac{(J-2)(J+1)(2J-3)^2(2J+1)(2J+3)}{4(J-1)J^2(2J-1)^2}$
$Q_3(J)$	$\frac{2J+1}{4J(J+1)}$	$\frac{(2J-5)^2(2J+3)}{128(J-1)J(J+1)^2}$	$\frac{4(2J^2+J-9)^2}{(J+1)(2J-1)^2(2J+1)}$
$R_3(J)$	$\frac{(2J+1)(2J+3)}{4(J+1)}$	$\frac{(2J-5)^2(2J+3)^2}{128(J-1)(J+1)^2}$	$\frac{(J-1)(J+2)(2J-1)^2(2J+3)(2J+5)}{4J(J+1)^2(2J+1)^2}$
$P_4(J)$	$\frac{(2J-3)(2J+3)}{4J}$	$\frac{(2J-3)(4J^2-4J-39)^2}{128J^2(J+2)(2J+1)}$	$\frac{(J-1)(J+2)(2J-3)(2J-1)(2J+3)^2}{4J^2(J+1)(2J+1)^2}$
$Q_4(J)$	$\frac{9(2J+1)}{4J(J+1)}$	$\frac{9(4J^2-4J-39)^2}{128J^2(J+1)(J+2)(2J+3)}$	$\frac{4(2J^2+3J-8)^2}{J(J+1)(2J+1)(2J+3)^2}$

$R_4(J)$	$\frac{(2J-1)(2J+5)}{4(J+1)}$	$\frac{(2J-1)(2J+5)(4J^2-4J-39)^2}{128J(J+1)(J+2)(2J+1)(2J+3)}$	$\frac{J(J+3)(2J-1)(2J+1)(2J+5)^2}{4(J+1)^2(J+2)(2J+3)^2}$
$P_5(J)$	$\frac{(2J-5)(2J+5)}{4J}$	$\frac{(2J-5)(2J-3)(2J-1)(6J+25)^2}{512J^2(J+1)(2J+3)}$	$\frac{(J-1)(2J-1)(2J+1)(2J+5)^2}{4J(J+1)(2J+3)^2}$
$Q_5(J)$	$\frac{25(2J+1)}{4J(J+1)}$	$\frac{25(2J-3)(2J-1)(2J+1)(6J+25)^2}{512J^2(J+1)^2(2J+3)(2J+5)}$	$\frac{4(2J+1)(2J^2+5J-5)^2}{J(J+1)(2J+3)^2(2J+5)^2}$
$R_3(J)$	$\frac{(2J-3)(2J+7)}{4(J+1)}$	$\frac{(2J-3)^2(2J-1)(2J+7)(6J+25)^2}{512J(J+1)^2(2J+3)(2J+5)}$	$\frac{J(2J+1)(2J+3)(2J+7)^2}{4(J+1)(J+2)(2J+5)^2}$
$P_6(J)$	$\frac{(2J-7)(2J+7)}{4J}$	$\frac{(2J-7)(2J-5)(2J-3)(2J-1)(2J+7)}{512J(J+1)(J+2)(2J+5)}$	$\frac{(2J-1)(2J+3)(2J+7)}{4(J+2)(2J+5)}$
$Q_6(J)$	$\frac{49(2J+1)}{4J(J+1)}$	$\frac{49(2J-5)(2J-3)(2J-1)(2J+1)}{512J(J+1)^2(J+2)(2J+5)}$	$\frac{4J(2J+1)}{(J+1)(2J+5)^2}$
$R_6(J)$	$\frac{(2J-5)(2J+9)}{4(J+1)}$	$\frac{(2J-5)^2(2J-3)(2J+1)(2J+9)}{512(J+1)^2(J+2)(2J+5)}$	$\frac{(2J+1)(2J+5)(2J+9)}{4(J+3)(2J+7)}$
$KP_{16}(J)$	0	$\frac{(2J-3)(2J-1)(2J+3)(2J+7)}{512J(J+1)(J+2)}$	0
$LP_{26}(J)$	0	$\frac{5(2J-1)(2J+1)(2J+3)(2J+7)}{512J(J+1)(J+2)}$	0
$MP_{36}(J)$	0	$\frac{5(2J-1)(2J+1)(2J+3)(2J+7)}{256J(J+1)(J+2)}$	0
$NP_{46}(J)$	0	$\frac{5(2J-3)(2J-1)(2J+3)(2J+7)}{256J(J+1)(J+2)}$	0

Table 3.19 (continued)

Branches	Line strengths		
	${}^6\Pi(a) - {}^6\Pi(a)$	${}^6\Pi(a) - {}^6\Pi(b)$	${}^6\Pi(b) - {}^6\Pi(b)$
${}^oP_{36}(J)$	0	$\frac{5(2J-5)(2J-3)(2J-1)(2J+7)}{512(J+1)(J+2)}$	0
${}^pQ_{36}(J)$	0	$\frac{125(2J-3)(2J-1)(2J+1)(2J+7)}{512(J+1)^2(J+2)(2J+5)}$	$\frac{5(2J+1)(2J+3)(2J+7)}{4(J+1)(J+2)(2J+5)^2}$
${}^RQ_{31}(J)$	0	$\frac{5(2J-5)(2J-1)(2J+1)}{512(J-1)J^2(J+1)}$	$\frac{5(2J-5)(2J-1)(2J+1)}{4(J-1)J(2J-3)^2}$
${}^SR_{31}(J)$	0	$\frac{5(2J-5)(2J-1)(2J+1)(2J+3)}{512(J-1)J(J+1)}$	0
${}^TR_{31}(J)$	0	$\frac{5(2J-5)(2J-1)(2J+1)(2J+3)}{256(J-1)J(J+1)}$	0
${}^UP_{11}(J)$	0	$\frac{5(2J-5)(2J-1)(2J+3)(2J+5)}{256(J-1)J(J+1)}$	0
${}^VR_{51}(J)$	0	$\frac{5(2J-5)(2J+3)(2J+5)(2J+7)}{512(J-1)J(J+1)}$	0
${}^WR_{61}(J)$	0	$\frac{(2J-5)(2J+3)(2J+5)(2J+7)(2J+9)}{512(J-1)J(J+1)(2J-3)}$	0

Table 3.20. Line Strengths for ${}^6\Pi - {}^6\Sigma$ Transitions

Branches		Line strengths	
${}^6\Pi - {}^6\Sigma$	${}^6\Sigma - {}^6\Pi$	${}^6\Pi(a) - {}^6\Sigma$	${}^6\Pi(b) - {}^6\Sigma$
$P_1(J)$	$R_1(J-1)$	$\frac{(2J+3)^2 (2J+5)^2}{1024(J-1)J^2}$	$\frac{(2J-7)(2J+1)}{8(J-2)}$
$Q_1(J)$	$Q_1(J)$	$\frac{(2J-3)(2J+1)(2J+3)(2J+5)^2}{1024(J-1)J^2(J+1)}$	$\frac{(J+1)(2J-5)(2J+1)}{2J(2J-3)}$
$R_1(J)$	$P_1(J+1)$	$\frac{(2J-3)(2J-1)(2J+3)(2J+5)}{1024(J-1)J(J+1)}$	$\frac{(2J-1)(2J+3)}{8(J-1)}$
$P_2(J)$	$R_2(J-1)$	$\frac{9(2J-3)(2J+1)(2J+3)^2}{1024J^2(J+1)}$	$\frac{(J+1)(2J-5)^2(2J+1)}{8(J-1)J(2J-3)}$
$Q_2(J)$	$Q_2(J)$	$\frac{9(2J-3)(2J-1)(2J+1)(2J+3)^2}{1024J^2(J+1)^2}$	$\frac{(2J+1)(2J^2-J-8)^2}{2J(J+1)(2J-3)(2J-1)}$
$R_2(J)$	$P_2(J+1)$	$\frac{9(2J-3)(2J-1)(2J+1)(2J+3)}{1024J(J+1)^2}$	$\frac{(J+2)(2J-3)(2J+1)(2J+3)}{8J(J+1)(2J-1)}$
$P_3(J)$	$R_3(J-1)$	$\frac{(2J-1)^2(2J+1)(2J+3)}{256(J-1)J(J+1)}$	$\frac{(J-2)(J+1)(2J-3)^2(2J+3)}{8(J-1)J^2(2J-1)}$
$Q_3(J)$	$Q_3(J)$	$\frac{(2J-1)(2J+1)^3(2J+3)}{256(J-1)J(J+1)^2}$	$\frac{(2J^2+J-9)^2}{2J(J+1)(2J-1)}$
$R_3(J)$	$P_3(J+1)$	$\frac{(2J-1)(2J+1)(2J+3)^2}{256(J-1)(J+1)^2}$	$\frac{(J-1)(J+2)(2J-1)(2J+3)(2J+5)}{8J(J+1)^2(2J+1)}$
$P_4(J)$	$R_4(J-1)$	$\frac{(2J-3)(2J-1)^2(2J+3)}{256J^2(J+2)}$	$\frac{(J-1)(J+2)(2J-3)(2J-1)(2J+3)}{8J^2(J+1)(2J+1)}$
$Q_4(J)$	$Q_4(J)$	$\frac{(2J-1)^2(2J+1)(2J+3)^2}{256J^2(J+1)(J+2)}$	$\frac{(2J^2+3J-8)^2}{2J(J+1)(2J+3)}$
$R_4(J)$	$P_4(J+1)$	$\frac{(2J-1)(2J+3)^2(2J+5)}{256J(J+1)(J+2)}$	$\frac{J(J+3)(2J-1)(2J+5)^2}{8(J+1)^2(J+2)(2J+3)}$
$P_5(J)$	$R_5(J-1)$	$\frac{9(2J-5)(2J-3)(2J-1)(2J+5)}{1024J^2(J+1)}$	$\frac{(J-1)(2J-1)(2J+1)(2J+5)}{8J(J+1)(2J+3)}$
$Q_5(J)$	$Q_5(J)$	$\frac{9(2J-3)(2J-1)(2J+1)(2J+5)^2}{1024J^2(J+1)^2}$	$\frac{(2J+1)(2J^2+5J-5)^2}{2J(J+1)(2J+3)(2J+5)}$
$R_5(J)$	$P_5(J+1)$	$\frac{9(2J-1)(2J+5)^2(2J+7)}{1024J(J+1)^2}$	$\frac{J(2J+1)(2J+7)^2}{8(J+1)(J+2)(2J+5)}$
$P_6(J)$	$R_6(J-1)$	$\frac{(2J-7)(2J-5)(2J-3)(2J-1)}{1024J(J+1)(J+2)}$	$\frac{(2J-1)(2J+3)}{8(J+2)}$
$Q_6(J)$	$Q_6(J)$	$\frac{(2J-5)(2J-3)(2J-1)(2J+1)(2J+7)}{1024J(J+1)^2(J+2)}$	$\frac{J(2J+1)(2J+7)}{2(J+1)(2J+5)}$

Table 3.20 (continued)

Branches		Line strengths	
${}^6\Pi-{}^6\Sigma$	${}^6\Sigma-{}^6\Pi$	${}^6\Pi(a)-{}^6\Sigma$	${}^6\Pi(b)-{}^6\Sigma$
$R_6(J)$	$P_6(J+1)$	$\frac{(2J-3)(2J-1)(2J+7)(2J+9)}{1024(J+1)^2(J+2)}$	$\frac{(2J+1)(2J+9)}{8(J+3)}$
$KP_{16}(J)$	${}^WR_{61}(J-1)$	$\frac{(2J-3)(2J-1)(2J+3)(2J+5)}{1024J(J+1)(J+2)}$	0
$LP_{26}(J)$	${}^VR_{62}(J-1)$	$\frac{5(2J-1)(2J+1)(2J+3)(2J+5)}{1024J(J+1)(J+2)}$	0
$MP_{36}(J)$	${}^UR_{63}(J-1)$	$\frac{5(2J-1)(2J+1)(2J+3)(2J+5)}{512J(J+1)(J+2)}$	0
$NP_{46}(J)$	${}^TR_{64}(J-1)$	$\frac{5(2J-3)(2J-1)(2J+3)(2J+5)}{512J(J+1)(J+2)}$	0
$OP_{56}(J)$	${}^SR_{65}(J-1)$	$\frac{5(2J-5)(2J-3)(2J-1)(2J+5)}{1024J(J+1)(J+2)}$	0
$PQ_{56}(J)$	${}^RQ_{65}(J)$	$\frac{5(2J-3)(2J-1)(2J+1)(2J+5)^2}{1024J(J+1)^2(J+2)}$	$\frac{5(2J+1)(2J+3)}{8(J+1)(J+2)(2J+5)}$
$RQ_{21}(J)$	${}^PQ_{12}(J)$	$\frac{5(2J-3)(2J-1)(2J+1)(2J+3)^2}{1024(J-1)J^2(J+1)}$	$\frac{5(2J-1)(2J+1)}{8(J-1)J(2J-3)}$
$SR_{21}(J)$	${}^OP_{12}(J+1)$	$\frac{5(2J-3)(2J-1)(2J+1)(2J+3)}{1024(J-1)J(J+1)}$	0
$TR_{31}(J)$	${}^NP_{13}(J+1)$	$\frac{5(2J-3)(2J-1)(2J+1)(2J+3)}{512(J-1)J(J+1)}$	0
$UR_{41}(J)$	${}^MP_{14}(J+1)$	$\frac{5(2J-3)(2J-1)(2J+3)(2J+5)}{512(J-1)J(J+1)}$	0
$VR_{51}(J)$	${}^LP_{15}(J+1)$	$\frac{5(2J-3)(2J+3)(2J+5)(2J+7)}{1024(J-1)J(J+1)}$	0
$WR_{61}(J)$	${}^KP_{16}(J+1)$	$\frac{(2J+3)(2J+5)(2J+7)(2J+9)}{1024(J-1)J(J+1)}$	0

Kleman and Uhler [93] observed a ${}^6\Sigma-{}^6\Sigma$ transition in the CrH molecule, but did not report intensity data. They found only the main branch 12, and none of the very weak sub-branches.

3.2.7. Septet Transitions

The transformation-matrix elements necessary for the calculation of the line strengths of septet transitions are the following.

${}^7\Sigma(\mathbf{b})$ transformation matrix (Kovács [103])

$$\begin{aligned}
S_{\mp 3, J-3} &= \sqrt{\frac{(J+1)(J+2)(J+3)}{8(2J-3)(2J-1)(2J+1)}} \\
S_{\mp 2, J-3} &= -\sqrt{\frac{6(J-1)(J+1)(J+2)}{8(2J-3)(2J-1)(2J+1)}} \\
S_{\mp 1, J-3} &= \sqrt{\frac{15(J-2)(J-1)(J+1)}{8(2J-3)(2J-1)(2J+1)}} \\
S_{0, J-3} &= -\sqrt{\frac{20(J-2)(J-1)J}{8(2J-3)(2J-1)(2J+1)}} \\
S_{\mp 3, J-2} &= \pm \sqrt{\frac{3(J+2)(J+3)}{8(2J-1)(2J+1)}} \\
S_{\mp 2, J-2} &= \mp \sqrt{\frac{8(J-2)(J+2)}{8(2J-1)(2J+1)}} \\
S_{\mp 1, J-2} &= \pm \sqrt{\frac{5(J-2)(J-1)}{8(2J-1)(2J+1)}}; \quad S_{0, J-2} = 0 \\
S_{\mp 3, J-1} &= \sqrt{\frac{15(J-2)(J+2)(J+3)}{8(2J-3)(2J+1)(2J+3)}} \\
S_{\mp 2, J-1} &= -\sqrt{\frac{10(J-3)^2(J+2)}{8(2J-3)(2J+1)(2J+3)}} \\
S_{\mp 1, J-1} &= -\sqrt{\frac{(J-1)(J+6)^2}{8(2J-3)(2J+1)(2J+3)}} \\
S_{0, J-1} &= \sqrt{\frac{12(J-1)J(J+1)}{8(2J-3)(2J+1)(2J+3)}} \\
S_{\mp 3, J} &= \pm \sqrt{\frac{10(J-2)(J+3)}{8(2J-1)(2J+3)}}
\end{aligned} \tag{1}$$

$$S_{\mp 2, J} = \pm \sqrt{\frac{60}{8(2J-1)(2J+3)}}$$

$$S_{\mp 1, J} = \mp \sqrt{\frac{6(J-1)(J+2)}{8(2J-1)(2J+3)}}; \quad S_{0, J} = 0$$

$$S_{\mp 3, J+1} = \sqrt{\frac{15(J-2)(J-1)(J+3)}{8(2J-1)(2J+1)(2J+5)}}$$

$$S_{\mp 2, J+1} = \sqrt{\frac{10(J-1)(J+4)^2}{8(2J-1)(2J+1)(2J+5)}}$$

$$S_{\mp 1, J+1} = -\sqrt{\frac{(J-5)^2(J+2)}{8(2J-1)(2J+1)(2J+5)}}$$

$$S_{0, J+1} = -\sqrt{\frac{12J(J+1)(J+2)}{8(2J-1)(2J+1)(2J+5)}}$$

$$S_{\mp 3, J+2} = \pm \sqrt{\frac{3(J-2)(J-1)}{8(2J+1)(2J+3)}}$$

$$S_{\mp 2, J+2} = \pm \sqrt{\frac{8(J-1)(J+3)}{8(2J+1)(2J+3)}}$$

$$S_{\mp 1, J+2} = \pm \sqrt{\frac{5(J+2)(J+3)}{8(2J+1)(2J+3)}}; \quad S_{0, J+2} = 0$$

$$S_{\mp 3, J+3} = \sqrt{\frac{(J-2)(J-1)J}{8(2J+1)(2J+3)(2J+5)}}$$

$$S_{\mp 2, J+3} = \sqrt{\frac{6(J-1)J(J+3)}{8(2J+1)(2J+3)(2J+5)}}$$

$$S_{\mp 1, J+3} = \sqrt{\frac{15J(J+2)(J+3)}{8(2J+1)(2J+3)(2J+5)}}$$

$$S_{0,J+3} = \sqrt{\frac{20(J+1)(J+2)(J+3)}{8(2J+1)(2J+3)(2J+5)}}$$

7II((b) transformation matrix (Kovács, Scari [127])

$$S_{-2,J-3} = + \sqrt{\frac{(J-3)(J+1)(J+2)}{8(2J-3)(2J-1)(2J+1)}}$$

$$S_{-1,J-3} = - \sqrt{\frac{3(J-3)(J-1)(J+1)}{4(2J-3)(2J-1)(2J+1)}}$$

$$S_{0,J-3} = + \sqrt{\frac{15(J-3)(J-1)J}{8(2J-3)(2J-1)(2J+1)}}$$

$$S_{1,J-3} = - \sqrt{\frac{5(J-3)(J-1)(J+1)}{2(2J-3)(2J-1)(2J+1)}}$$

$$S_{2,J-3} = + \sqrt{\frac{15(J-3)(J+1)(J+2)}{8(2J-3)(2J-1)(2J+1)}}$$

$$S_{3,J-3} = - \sqrt{\frac{3(J-3)(J+1)(J+2)(J+3)}{4(J-2)(2J-3)(2J-1)(2J+1)}}$$

$$S_{4,J-3} = + \sqrt{\frac{(J+1)(J+2)(J+3)(J+4)}{8(J-2)(2J-3)(2J-1)(2J+1)}}$$

$$S_{-2,J-2} = + \sqrt{\frac{3(J-1)(J+2)}{8(2J-1)(2J+1)}}$$

$$S_{-1,J-2} = - \sqrt{\frac{2J-1}{4(2J+1)}} \quad (2)$$

$$S_{0,J-2} = + \sqrt{\frac{5J(J+1)}{8(2J-1)(2J+1)}}$$

$$S_{1,J-2} = - \sqrt{\frac{15}{2(2J-1)(2J+1)}}$$

$$S_{2,J-2} = - \sqrt{\frac{5(J-5)^2 (J+2)}{8(J-1) (2J-1) (2J+1)}}$$

$$S_{3,J-2} = + \sqrt{\frac{(J+2) (J+3) (2J-7)^2}{4(J-2) (J-1) (2J-1) (2J+1)}}$$

$$S_{4,J-2} = - \sqrt{\frac{3(J-3) (J+2) (J+3) (J+4)}{8(J-2) (J-1) (2J-1) (2J+1)}}$$

$$S_{-2,J-1} = + \sqrt{\frac{15(J-1) J(J+2)}{8(2J-3) (2J+1) (2J+3)}}$$

$$S_{-1,J-1} = - \sqrt{\frac{5J^3}{4(2J-3) (2J+1) (2J+3)}}$$

$$S_{0,J-1} = - \sqrt{\frac{(J-6)^2 (J+1)}{8(2J-3) (2J+1) (2J+3)}}$$

$$S_{1,J-1} = + \sqrt{\frac{3(J^2-6)^2}{2J(2J-3) (2J+1) (2J+3)}}$$

$$S_{2,J-1} = - \sqrt{\frac{(J+2) (J^2+15J-36)^2}{8(J-1) J(2J-3) (2J+1) (2J+3)}}$$

$$S_{3,J-1} = - \sqrt{\frac{5(J-6)^2 (J-2) (J+2) (J+3)}{4(J-1) J(2J-3) (2J+1) (2J+3)}}$$

$$S_{4,J-1} = + \sqrt{\frac{15(J-3) (J-2) (J+2) (J+3) (J+4)}{8(J-1) J(2J-3) (2J+1) (2J+3)}}$$

$$S_{-2,J} = + \sqrt{\frac{5J(J+1)}{4(2J-1) (2J+3)}}; \quad S_{-1,J} = 0$$

$$S_{0,J} = - \sqrt{\frac{3(J-1) (J+2)}{4(2J-1) (2J+3)}}$$

$$S_{1,J} = + \sqrt{\frac{9(J-1)(J+2)}{J(J+1)(2J-1)(2J+3)}}$$

$$S_{2,J} = + \sqrt{\frac{3(J-3)^2(J+4)^2}{4J(J+1)(2J-1)(2J+3)}}$$

$$S_{3,J} = - \sqrt{\frac{30(J-2)(J+3)}{J(J+1)(2J-1)(2J+3)}}$$

$$S_{4,J} = - \sqrt{\frac{5(J-3)(J-2)(J+3)(J+4)}{4J(J+1)(2J-1)(2J+3)}}$$

$$S_{-2,J+1} = + \sqrt{\frac{15(J-1)(J+1)(J+2)}{8(2J-1)(2J+1)(2J+5)}}$$

$$S_{-1,J+1} = + \sqrt{\frac{5(J+1)^3}{4(2J-1)(2J+1)(2J+5)}}$$

$$S_{0,J+1} = - \sqrt{\frac{J(J+7)^2}{8(2J-1)(2J+1)(2J+5)}}$$

$$S_{1,J+1} = - \sqrt{\frac{3(J^2+2J-5)^2}{2(J+1)(2J-1)(2J+1)(2J+5)}}$$

$$S_{2,J+1} = - \sqrt{\frac{(J-1)(J^2-13J-50)^2}{8(J+1)(J+2)(2J-1)(2J+1)(2J+5)}}$$

$$S_{3,J+1} = + \sqrt{\frac{5(J-2)(J-1)(J+3)(J+7)^2}{4(J+1)(J+2)(2J-1)(2J+1)(2J+5)}}$$

$$S_{4,J+1} = + \sqrt{\frac{15(J-3)(J-2)(J-1)(J+3)(J+4)}{8(J+1)(J+2)(2J-1)(2J+1)(2J+5)}}$$

$$S_{-2,J+2} = + \sqrt{\frac{3(J-1)(J+2)}{8(2J+1)(2J+3)}}$$

$$S_{-1,J+2} = + \sqrt{\frac{2J+3}{4(2J+1)}}$$

$$S_{0,J+2} = + \sqrt{\frac{5J(J+1)}{8(2J+1)(2J+3)}}$$

$$S_{1,J+2} = - \sqrt{\frac{15}{2(2J+1)(2J+3)}}$$

$$S_{2,J+2} = - \sqrt{\frac{5(J-1)(J+6)^2}{8(J+2)(2J+1)(2J+3)}}$$

$$S_{3,J+2} = - \sqrt{\frac{(J-2)(J-1)(2J+9)^2}{4(J+2)(J+3)(2J+1)(2J+3)}}$$

$$S_{4,J+2} = - \sqrt{\frac{3(J-3)(J-2)(J-1)(J+4)}{8(J+2)(J+3)(2J+1)(2J+3)}}$$

$$S_{-2,J+3} = + \sqrt{\frac{(J-1)J(J+4)}{8(2J+1)(2J+3)(2J+5)}}$$

$$S_{-1,J+3} = + \sqrt{\frac{3J(J+2)(J+4)}{4(2J+1)(2J+3)(2J+5)}}$$

$$S_{0,J+3} = + \sqrt{\frac{15(J+1)(J+2)(J+4)}{8(2J+1)(2J+3)(2J+5)}}$$

$$S_{1,J+3} = + \sqrt{\frac{5J(J+2)(J+4)}{2(2J+1)(2J+3)(2J+5)}}$$

$$S_{2,J+3} = + \sqrt{\frac{15(J-1)J(J+4)}{8(2J+1)(2J+3)(2J+5)}}$$

$$S_{3,J+3} = + \sqrt{\frac{3(J-2)(J-1)(J+4)}{4(J+3)(2J+1)(2J+3)(2J+5)}}$$

$$S_{4,J+3} = + \sqrt{\frac{(J-3)(J-2)(J-1)J}{8(J+3)(2J+1)(2J+3)(2J+5)}}$$

Table 3.21. Line Strengths for ${}^7\Pi - {}^7\Sigma$ Transitions

Branches		Line strengths	
${}^7\Pi - {}^7\Sigma$	${}^7\Sigma - {}^7\Pi$	${}^7\Pi(a) - {}^7\Sigma$	${}^7\Pi(b) - {}^7\Sigma$
$P_1(J)$	$R_1(J-1)$	$\frac{(J+1)(J+2)^2(J+3)^2}{16J(2J-3)(2J-1)(2J+1)}$	$\frac{(J-4)(2J+1)}{2(2J-5)}$
$Q_1(J)$	$Q_1(J)$	$\frac{(J-2)(J+2)(J+3)^2}{16J(2J-3)(2J-1)}$	$\frac{(J-3)(J+1)(2J+1)}{2(J-1)J}$
$R_1(J)$	$P_1(J+1)$	$\frac{(J-2)(J-1)(J+2)(J+3)}{16(2J-3)(2J-1)(2J+1)}$	$\frac{(J-1)(2J+3)}{2(2J-3)}$
${}^Q P_{21}(J)$	${}^Q R_{12}(J-1)$	$\frac{3(J-2)(J+1)^2(J+2)^2}{8J(2J-3)(2J-1)(2J+1)}$	$\frac{3(2J+1)}{2(J-2)J}$
${}^R Q_{21}(J)$	${}^P Q_{12}(J)$	$\frac{3(J-2)(J-1)(J+2)^2}{8J(2J-3)(2J-1)}$	$\frac{3(J-1)(2J+1)}{2(J-2)J(2J-3)}$
${}^R P_{31}(J)$	${}^P R_{13}(J-1)$	$\frac{15(J-2)(J-1)J(J+1)^2}{16(2J-3)(2J-1)(2J+1)}$	$\frac{15(J-1)}{2(J-2)J(2J-5)(2J-3)}$
${}^P Q_{12}(J)$	${}^R Q_{12}(J)$	$\frac{3(J-2)(J+2)(J+3)^2}{16J(J+1)(2J-1)}$	$\frac{3(J-3)(2J+1)}{2(J-2)(2J-3)}$
${}^Q R_{12}(J)$	${}^Q P_{21}(J+1)$	$\frac{3(J-2)(J-1)(J+2)(J+3)}{16(J+1)(2J-1)(2J+1)}$	$\frac{3(2J+3)}{2(J-1)(J+2)}$
$P_2(J)$	$R_2(J-1)$	$\frac{(J-2)(J+1)(J+2)^2}{2J(2J-1)(2J+1)}$	$\frac{(J-3)^2(J+1)(2J+1)}{2(J-2)J(2J-3)}$
$Q_2(J)$	$Q_2(J)$	$\frac{(J-2)(J-1)(J+2)^2}{2J(J+1)(2J-1)}$	$\frac{(J^2-J-5)^2(2J+1)}{2(J-2)(J-1)J(J+1)}$
$R_2(J)$	$P_2(J+1)$	$\frac{(J-2)(J-1)J(J+2)}{2(J+1)(2J-1)(2J+1)}$	$\frac{(J-2)J(J+2)(2J+3)}{2(J-1)(J+1)(2J-1)}$
${}^Q P_{32}(J)$	${}^Q R_{23}(J-1)$	$\frac{5(J-2)(J-1)(J+1)}{16(2J-1)(2J+1)}$	$\frac{5(J+1)(2J-5)}{(J-2)(J-1)J}$
${}^R Q_{32}(J)$	${}^P Q_{23}(J)$	$\frac{5(J-2)(J-1)}{16(2J-1)}$	$\frac{5(J-2)(2J+1)(2J+3)}{2(J-1)(J+1)(2J-3)(2J-1)}$
${}^R P_{42}(J)$	${}^P R_{24}(J-1)$	0	$\frac{15}{(J-1)(2J-3)(2J-1)}$
${}^P R_{13}(J)$	${}^R P_{31}(J+1)$	$\frac{15(J-2)^2(J-1)(J+2)(J+3)}{16(J+1)(2J-3)(2J+1)(2J+3)}$	$\frac{15(J-2)}{2(J-1)(J+1)(2J-3)(2J-1)}$
${}^P Q_{23}(J)$	${}^R Q_{32}(J)$	$\frac{5(J-3)^2(J-1)(J+2)^2}{8J(J+1)(2J-3)(2J+3)}$	$\frac{5(J-2)^2(2J+1)(2J+3)}{2(J-1)J(J+1)(2J-3)(2J-1)}$
${}^Q R_{23}(J)$	${}^Q P_{32}(J+1)$	$\frac{5(J-3)^2(J-1)J(J+2)}{8(J+1)(2J-3)(2J+1)(2J+3)}$	$\frac{5(J+2)(2J-3)}{2(J-1)J(J+1)}$

Table 3.21 (continued)

Branches		Line strengths	
${}^1\Pi - {}^1\Sigma$	${}^1\Sigma - {}^1\Pi$	${}^1\Pi(a) - {}^1\Sigma$	${}^1\Pi(b) - {}^1\Sigma$
$P_3(J)$	$R_3(J-1)$	$\frac{(J-1)(J+1)(J+6)^2}{16(2J-3)(2J+1)(2J+3)}$	$\frac{(J-2)^2(J+1)(2J-5)(2J+3)}{2(J-1)J(2J-3)(2J-1)}$
$Q_3(J)$	$Q_3(J)$	$\frac{(J-1)(J+6)^2}{16(2J-3)(2J+3)}$	$\frac{(J^2-6)^2(2J+1)}{2(J-1)J^2(J+1)}$
$R_3(J)$	$P_3(J+1)$	$\frac{(J-1)J(J+6)^2}{16(2J-3)(2J+1)(2J+3)}$	$\frac{(J-1)(J+2)(2J-3)(2J+5)}{2J(2J-1)(2J+1)}$
${}^Q P_{43}(J)$	${}^Q R_{34}(J-1)$	$\frac{3(J-1)^2 J(J+1)}{4(2J-3)(2J+1)(2J+3)}$	$\frac{3(J-2)(2J-3)}{(J-1)J^2}$
${}^R Q_{43}(J)$	${}^P Q_{34}(J)$	$\frac{3(J-1)J(J+1)}{4(2J-3)(2J+3)}$	$\frac{3(J+2)(2J-3)}{J^2(2J-1)}$
${}^R P_{53}(J)$	${}^P R_{35}(J-1)$	$\frac{(J-2)(J-1)^2(J+6)^2}{16J(2J-3)(2J+1)(2J+3)}$	$\frac{18(J+1)}{J^2(2J-1)(2J+1)}$
${}^P R_{24}(J)$	${}^R P_{42}(J+1)$	$\frac{15(J-1)J}{4(J+1)(2J-1)(2J+3)}$	$\frac{15(J-1)}{J(J+1)(2J-1)(2J+1)}$
${}^P Q_{34}(J)$	${}^R Q_{43}(J)$	$\frac{3(J-1)(J+2)(2J+1)}{8(2J-1)(2J+3)}$	$\frac{3(J-1)(J+2)(2J-3)}{J^2(J+1)(2J-1)}$
${}^Q R_{34}(J)$	${}^Q P_{43}(J+1)$	$\frac{3(J-1)J(J+2)}{8(2J-1)(2J+3)}$	$\frac{3(J-1)(2J+5)}{J(J+1)^2}$
$P_4(J)$	$R_4(J-1)$	0	$\frac{(J-2)(J-1)(J+2)(2J-3)(2J+3)}{2J^2(2J-1)(2J+1)}$
$Q_4(J)$	$Q_4(J)$	0	$\frac{(J-2)^2(J+3)^2(2J+1)}{2J^2(J+1)^2}$
$R_4(J)$	$P_4(J+1)$	0	$\frac{(J-1)(J+2)(J+3)(2J-1)(2J+5)}{2(J+1)^2(2J+1)(2J+3)}$
${}^Q P_{54}(J)$	${}^Q R_{45}(J-1)$	$\frac{3(J-2)(J-1)^2(J+2)}{8J(2J-1)(2J+3)}$	$\frac{3(J+2)(2J-3)}{2J^2(J+1)}$
${}^R Q_{54}(J)$	${}^P Q_{45}(J)$	$\frac{3(J-1)^2(J+2)^2(2J+1)}{8J(J+1)(2J-1)(2J+3)}$	$\frac{3(J-1)(J+2)(2J+5)}{J(J+1)^2(2J+3)}$
${}^R P_{64}(J)$	${}^P R_{46}(J-1)$	$\frac{15(J-3)(J-2)}{4J(2J-1)(2J+3)}$	$\frac{15(J+2)}{J(J+1)(2J+1)(2J+3)}$
${}^P R_{35}(J)$	${}^R P_{53}(J+1)$	$\frac{(J-5)^2 J(J+2)}{16(2J-1)(2J+1)(2J+5)}$	$\frac{18J}{(J+1)^2(2J+1)(2J+3)}$
${}^P Q_{45}(J)$	${}^R Q_{54}(J)$	$\frac{3J(J+1)(J+2)}{4(2J-1)(2J+5)}$	$\frac{3(J-1)(2J+5)}{(J+1)^2(2J+3)}$

Table 3.21 (continued)

Branches		Line strengths	
${}^1\Pi-{}^1\Sigma$	${}^1\Sigma-{}^1\Pi$	${}^1\Pi(a)-{}^1\Sigma$	${}^1\Pi(b)-{}^1\Sigma$
${}^Q R_{45}(J)$	${}^Q P_{54}(J+1)$	$\frac{3J(J+1)(J+2)^2}{4(2J-1)(2J+1)(2J+5)}$	$\frac{3(J+3)(2J+1)}{(J+1)^2(J+2)}$
$P_5(J)$	$R_5(J-1)$	$\frac{(J-5)^2(J-2)(J-1)(J+2)}{16J(2J-1)(2J+1)(2J+5)}$	$\frac{(J-1)(J+2)(2J-3)(2J+5)}{2(J+1)(2J+1)(2J+3)}$
$Q_5(J)$	$Q_3(J)$	$\frac{(J-5)^2(J-1)(J+2)^2}{16J(J+1)(2J-1)(2J+5)}$	$\frac{(J^2+2J-5)^2(2J+1)}{2J(J+1)^2(J+2)}$
$R_5(J)$	$P_5(J+1)$	$\frac{(J-5)^2(J+2)^2(J+3)}{16(J+1)(2J-1)(2J+1)(2J+5)}$	$\frac{J(J+3)^2(2J-1)(2J+7)}{2(J+1)(J+2)(2J+3)(2J+5)}$
${}^Q P_{65}(J)$	${}^Q R_{56}(J-1)$	$\frac{5(J-3)(J-2)(J-1)(J+4)^2}{8J(2J-1)(2J+1)(2J+5)}$	$\frac{5(J-1)(2J+5)}{2J(J+1)(J+2)}$
${}^R Q_{65}(J)$	${}^P Q_{56}(J)$	$\frac{5(J-2)(J-1)(J+3)(J+4)^2}{8J(2J+1)(2J-1)(2J+5)}$	$\frac{5(J+3)^2(2J-1)(2J+1)}{2J(J+1)(J+2)(2J+3)(2J+5)}$
${}^R P_{75}(J)$	${}^P R_{57}(J-1)$	$\frac{15(J-4)(J-3)(J-2)(J-1)(J+3)}{16J(2J-1)(2J+1)(2J+5)}$	$\frac{15(J+3)}{2J(J+2)(2J+3)(2J+5)}$
${}^P R_{46}(J)$	${}^R P_{64}(J+1)$	0	$\frac{15}{(J+2)(2J+3)(2J+5)}$
${}^P Q_{56}(J)$	${}^R Q_{65}(J)$	$\frac{5(J-1)(J+2)^2(J+3)}{16J(J+1)(2J+3)}$	$\frac{5(J+3)(2J-1)(2J+1)}{2J(J+2)(2J+3)(2J+5)}$
${}^Q R_{56}(J)$	${}^Q P_{65}(J+1)$	$\frac{5(J+2)^2(J+3)^2}{16(J+1)(2J+1)(2J+3)}$	$\frac{5J(2J+7)}{2(J+1)(J+2)(J+3)}$
$P_6(J)$	$R_6(J-1)$	$\frac{(J-3)(J-2)(J-1)(J+3)}{2J(2J+1)(2J+3)}$	$\frac{(J-1)(J+1)(J+3)(2J-1)}{2J(J+2)(2J+3)}$
$Q_6(J)$	$Q_6(J)$	$\frac{(J-2)(J-1)(J+3)^2}{2J(J+1)(2J+3)}$	$\frac{(J^2+3J-3)^2(2J+1)}{2J(J+1)(J+2)(J+3)}$
$R_6(J)$	$P_6(J+1)$	$\frac{(J-1)(J+3)^2(J+4)}{2(J+1)(2J+1)(2J+3)}$	$\frac{J(J+4)^2(2J+1)}{2(J+1)(J+3)(2J+5)}$
${}^Q P_{76}(J)$	${}^Q R_{67}(J-1)$	$\frac{3(J-4)(J-3)(J-2)(J-1)}{16J(2J+1)(2J+3)}$	$\frac{3(2J-1)}{2J(J+1)}$
${}^R Q_{76}(J)$	${}^P Q_{67}(J)$	$\frac{3(J-3)(J-2)(J-1)(J+4)}{16J(J+1)(2J+3)}$	$\frac{3(J+4)(2J+1)}{2(J+1)(J+3)(2J+5)}$
${}^P R_{57}(J)$	${}^R P_{75}(J+1)$	$\frac{15J(J+2)^2(J+3)^2}{16(J+1)(2J+1)(2J+3)(2J+5)}$	$\frac{15(J+2)}{2(J+1)(J+3)(2J+5)(2J+7)}$
${}^P Q_{67}(J)$	${}^R Q_{76}(J)$	$\frac{3(J-3)(J-2)(J-1)(J+4)}{8(J+1)(2J+3)(2J+5)}$	$\frac{3(J+2)(2J+1)}{2(J+1)(J+3)(2J+5)}$

Table 3.21 (continued)

Branches		Line strengths	
${}^7\Pi-{}^7\Sigma$	${}^7\Sigma-{}^7\Pi$	${}^7\Pi(a)-{}^7\Sigma$	${}^7\Pi(b)-{}^7\Sigma$
${}^Q R_{67}(J)$	${}^Q P_{76}(J+1)$	$\frac{3(J-2)(J-1)J(J+4)(J+5)}{8(J+1)(2J+1)(2J+3)(2J+5)}$	$\frac{3(2J+1)}{2(J+1)(2J+3)}$
$P_7(J)$	$R_7(J-1)$	$\frac{(J-4)(J-3)(J-2)(J-1)}{16(2J+1)(2J+3)(2J+5)}$	$\frac{(J+2)(2J-1)}{2(2J+5)}$
$Q_7(J)$	$Q_7(J)$	$\frac{(J-3)(J-2)(J-1)(J+4)}{16(J+1)(2J+3)(2J+5)}$	$\frac{J(J+4)(2J+1)}{2(J+1)(J+3)}$
$R_7(J)$	$P_7(J+1)$	$\frac{(J-2)(J-1)J(J+4)(J+5)}{16(J+1)(2J+1)(2J+3)(2J+5)}$	$\frac{(J+5)(2J+1)}{2(2J+7)}$

Using the above matrices, the line strengths for the limiting-case transitions ${}^7\Sigma-{}^7\Sigma$, ${}^7\Pi-{}^7\Pi$, ${}^7\Pi-{}^7\Sigma$ can be calculated [by Table 3.1 and by (3.2-3)]. Since the available experimental data suffice to verify only the line strengths of the last-mentioned transition, only these have been calculated (Kovács, Scari [127]). The ${}^7\Pi$ terms in Table 3.21 are normal. If an inverted term occurs instead of a normal one, then the suffixes corresponding to the inverted terms in the branch symbols have to be changed according to the pattern $1 \rightarrow 7$, $2 \rightarrow 6$, etc. wherever ${}^7\Pi(a)$ term occurs. In order to save space only 55 branches have been listed of the possible 147; for these the selection rules $\Delta J=0, \pm 1$ and $\Delta N=0, \pm 1$ hold, i.e. their line strengths are other than zero in case b.

The 0-0 band in the transition ${}^7\Pi-{}^7\Sigma$ of the MnH molecule as observed by Nevin [165, 166] served for an experimental verification. Kovács and Scari [127] confronted the ${}^7\Pi(b)-{}^7\Sigma$ line strengths calculated from Table 3.21 with the experimental data of Nevin; their results are shown in Fig. 3.8 below.

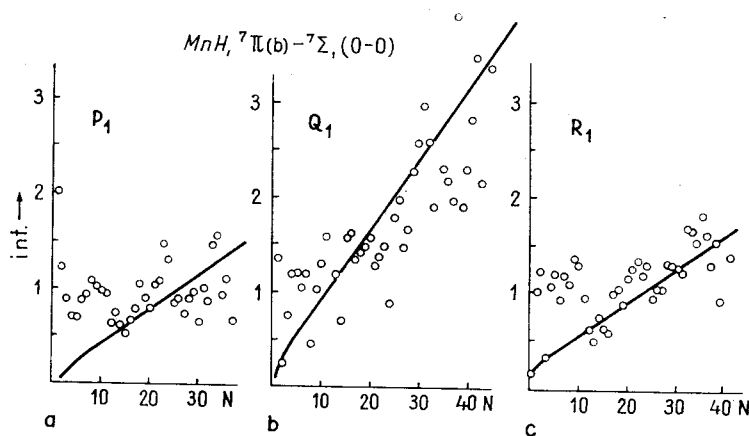


Fig. 3.8 (see p. 174)

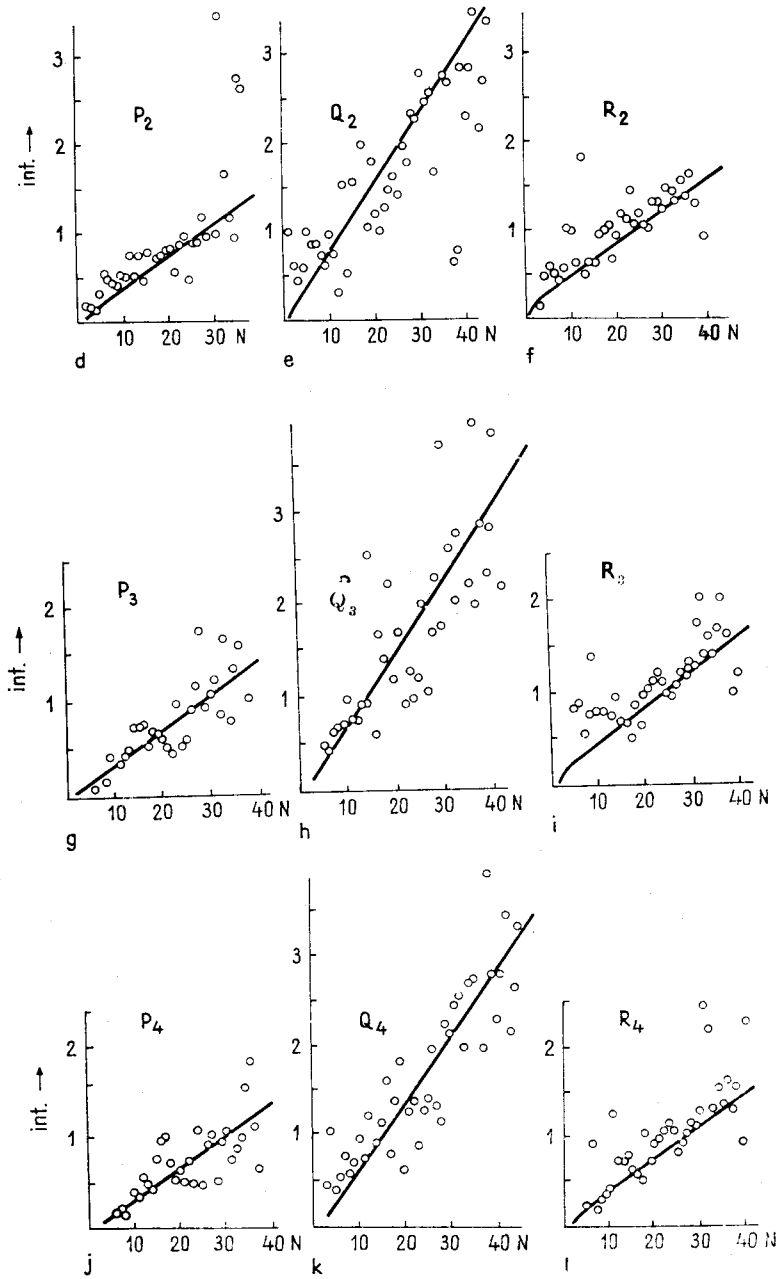


Fig. 3.8 (continued; see p. 174)

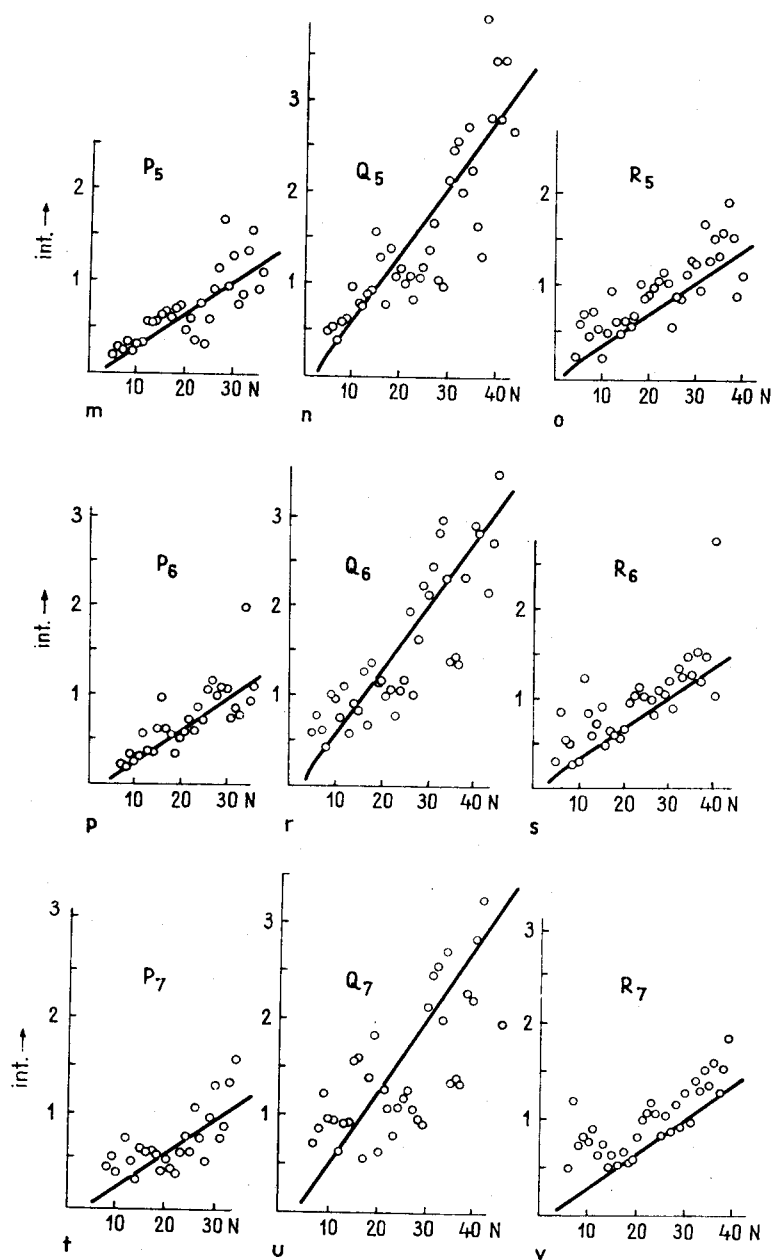


Fig. 3.8 Intensity distribution of the 0-0 bands in the transition ${}^7\Pi-{}^7\Sigma$ of the MnH molecule, according to Kovács and Scari [127], using formula (3.1-23).

The dispersion of the observed data in the figures is due to the circumstance that Nevin estimated his line intensities by eye rather than measuring them. Only the main-branch intensities are compared, since for quantum numbers high enough for satisfactory approximation by case *b* the satellite-branch line strengths are zero.

3.3. INTENSITY DISTRIBUTION AMONG SPIN MULTIPLETS OF DIFFERENT MULTIPLICITY

In the transitions discussed so far the selection rule $\Delta S = 0$ is strictly valid, which means that only transitions among terms of the same multiplicity are admitted. Experiments have shown, however, although less frequently, that transitions among terms of different multiplicity will also occur; these are called *intercombination* transitions. Such transitions have been observed between singlet and triplet terms and also between doublet and quartet terms. The theoretical interpretation, and the calculation of the line strengths, of intercombination transitions are based on taking into account the spin-orbit interaction. It is known that this interaction can entail perturbations also among terms of different multiplicity; cf. (1.2-7b) and (1.2-9b). As a result of this perturbation, the eigenfunctions of terms with the same Ω value and with $\Delta A = -\Delta \Sigma = 0, \pm 1, \Delta S = 0, \pm 1$ are 'mixed' (i.e. they form linear combinations). If the terms influencing one another are separated widely enough, then each term preserves its original character, which means that in the electronic parts of the eigenfunctions the 'foreign' terms occur with coefficients much smaller than unity. The new eigenfunctions will therefore be

$$\Phi_{S', A', \Sigma'} = \Phi_{S', A', \Sigma'} + \sum_{S'', A'', \Sigma''} C(S', A', \Sigma'; S'', A'', \Sigma'') \Phi_{S'', A'', \Sigma''} \quad (1)$$

where $\Phi_{S', A', \Sigma'}$ is the electronic part of the eigenfunction of the originally unperturbed term, $\Phi_{S'', A'', \Sigma''}$ is the electronic part of the new, perturbed eigenfunction, and

$$C(S', A', \Sigma'; S'', A'', \Sigma'') = \frac{H(S', A', \Sigma'; S'', A'', \Sigma'')}{v(S', A', \Sigma'; S'', A'', \Sigma'')} \quad (2)$$

where

$$H(S', A', \Sigma'; S'', A'', \Sigma'') = \int \Phi_{S', A', \Sigma'}^* \Sigma a_i(\mathbf{l}, \mathbf{s}_i) \Phi_{S'', A'', \Sigma''} d\tau \quad (3)$$

is the matrix element of the spin-orbit interaction, and v is the corresponding term spacing. The summation is to be extended over the terms $\Delta S = 0, \pm 1$ and $\Delta A = -\Delta \Sigma = 0, \pm 1$, but the condition $|S''| \geq |\Sigma''|$ is to be observed throughout.

Complementing these new electronic eigenfunctions by the corresponding vibrational and rotational eigenfunctions we obtain new eigenfunctions which are now to be substituted into the expression of the component R_z in formula (3.1-6). These new eigenfunctions will yield non-zero R_z values also for terms of different multiplicity.

One essential difference is to be noted, however, when these transitions are compared with those among terms of the same multiplicity. It is that in the transitions between the different components of two terms of the same multiplicity, (3.1-16) entails either only $\Delta\Omega = 0$ or only $\Delta\Omega = \pm 1$. Hence, in the final analysis, we obtain formulas similar to (3.1-15) not only in *Hund's case a* but also in the intermediate case between *Hund's cases a* and *b*, and in *Hund's case b*, i.e. even when making use of the eigenfunctions (3.2-1). In other words, the parts depending on the electron coordinates and on the rotational quantum number *can be separated* in the intensity formulas and so *the line strength can be defined*. On the other hand, in the case of transitions between terms of different multiplicity we have to substitute in Formula (3.1-10) for the ζ and η components of the electric transition moment $R_e^{n'n''}$ the *linear combinations* of the ζ and η components that correspond to the transitions between states in the linear combinations of the eigenfunctions. The linear combinations of the components generally differ from each other, since by $\Delta\Sigma = 0, \pm 1$, $\Delta\Omega = 0$ and $\Delta\Omega = \pm 1$ are now equally possible in transitions between multiplet components. In (3.2-2), obtained with the eigenfunctions (3.2-1) referring to case *b* or to the intermediate case between cases *a* and *b*, where now (1) will stand instead of the electronic part of ψ_a , even these will form further linear combinations which make it impossible, apart from some exceptional cases, to separate

$$S_{J'J''}^{n'n''} = \sum_M |R_{n''}^{n'J'}|^2 \quad (4)$$

into a part depending only on the rotational quantum number and one depending only on the electron coordinates, either in the intensity formulas corresponding to (3.1-15) or in the definitive formulas. Hence, in this case *no line strength* $S_{J'J''}$ depending only on the rotational quantum number *can be defined* (as contrary to the case discussed above). Instead, the values of the expressions (4) will be given in the subsequent tables, so that one constant will always be removed (without any special indication of the fact) and the number of the explicit constants will thus be reduced by one.

The application of the eigenfunctions (1) affects the selection rules, too. If only the small terms of the first order of magnitude are retained in each linear combination, then, in addition to the transitions $\Delta S = 0, \Delta I = 0, \pm 1$, permitted also in the preceding cases, the transitions $\Delta S = \pm 1$ and $\Delta I = \pm 2$ will also be possible. The selection rule $\Delta S = \pm 1$ serves to interpret the intercombination transitions, whereas $\Delta I = \pm 2$ explains e.g. the transitions $^3\Sigma^- \rightarrow ^3\Delta$ in Table 3.11. Additional transitions forbidden for symmetry reasons can also occur, e.g. the transitions $^3\Sigma^\pm \rightarrow ^3\Sigma^\mp$ in Table 3.9.

3.3.1. Singlet-Triplet Transitions

The procedure outlined above will now be applied to all possible transitions between the terms $^1\Sigma, ^1\Pi, ^1\Delta$ and $^3\Sigma, ^3\Pi, ^3\Delta$. Table 3.22 lists first of all the $S_{J'J''}^{n'n''}$ values in a corrected form for transitions involving the term

Table 3.22. Intensity Distribution for $^1\Sigma - ^3\Pi$ Triplet Transitions

$A' - A''$	$A'' - A'$	$^1\Sigma^{\pm'} - ^3\Sigma^{\pm''}$	$^1\Sigma^{\pm'} - ^3\Sigma^{\mp'}$	$^1\Sigma' - ^3\Pi''(\text{int})$	$^1\Sigma' - ^3A''(\text{int})$
$^oP(J)$	$^sR(J-1)$	0	$\frac{(\varrho-1)^2 J(J+1)}{2(2J+1)}$	$\frac{J^2(J+1)}{4C_3(J)} \{ \sigma u_3^-(J) - 2(J+2) \}^2$	$\frac{(J-1)(J+1)(J+2)}{8C_3(J)} u_3^-(J)^2$
$^pQ(J)$	$^rQ(J)$	$\frac{J}{2}$	0	$\frac{J^2(J+2)^2(2J+1)}{C_3(J)}$	$\frac{(J-1)(J+2)(2J+1)}{8C_3(J)} u_3^-(J)^2$
$^qR(J)$	$^qP(J+1)$	0	$\frac{(\varrho(J+1)+J)^2}{2(2J+1)}$	$\frac{J}{4C_3(J)} \{ (J+1) \sigma u_3^-(J) + 2J(J+2) \}^2$	$\frac{(J-1)J(J+2)}{8C_3(J)} u_3^-(J)^2$
$P(J)$	$R(J-1)$	$\frac{J+1}{2}$	0	$\frac{J+1}{2C_2(J)} \{ (Y-2) - 2\sigma J \}^2$	$\frac{(J-1)(J+1)(J+2)}{C_2(J)}$
$Q(J)$	$Q(J)$	0	$\frac{2J+1}{2}$	$\frac{2J+1}{2C_2(J)} (Y-2)^2$	$\frac{(J-1)(J+2)(2J+1)}{C_2(J)}$
$R(J)$	$P(J+1)$	$\frac{J}{2}$	0	$\frac{J}{2C_2(J)} \{ (Y-2) + 2\sigma(J+1) \}^2$	$\frac{(J-1)J(J+2)}{C_2(J)}$
$^qP(J)$	$^qR(J-1)$	0	$\frac{(\varrho(J+1)+1)^2}{2(2J+1)}$	$\frac{J+1}{4C_1(J)} \{ J \sigma u_1^+(J) + 2(J-1)(J+1) \}^2$	$\frac{(J-1)(J+1)(J+2)}{8C_1(J)} u_1^+(J)^2$
$^rQ(J)$	$^pQ(J)$	$\frac{J+1}{2}$	0	$\frac{(J-1)^2(J+1)^2(2J+1)}{C_1(J)}$	$\frac{(J-1)(J+2)(2J+1)}{8C_1(J)} u_1^+(J)^2$
$^sR(J)$	$^oP(J+1)$	0	$\frac{(\varrho-1)^2 J(J+1)}{2(2J+1)}$	$\frac{J(J+1)^2}{4C_1(J)} \{ \sigma u_1^+(J) - 2(J-1) \}^2$	$\frac{(J-1)J(J+2)}{8C_1(J)} u_1^+(J)^2$

$^1\Sigma$, i.e. for $^1\Sigma\text{--}^3\Sigma$, $^1\Sigma\text{--}^3\Pi$, $^1\Sigma\text{--}^3\Delta$. The values for the transitions $^1\Sigma\text{--}^3\Sigma$ (and also for the limiting-case transitions $^1\Sigma\text{--}^3\Pi(a)$, $^1\Sigma\text{--}^3\Pi(b)$, $^1\Sigma\text{--}^3\Delta(a)$, $^1\Sigma\text{--}^3\Delta(b)$, not listed in Table 3.22) were derived by Schlapp [193],* whereas the values for the intermediate-case transition $^1\Sigma\text{--}^3\Pi(\text{int})$ were reported by Budó [21], and those for $^1\Sigma\text{--}^3\Delta(\text{int})$ were given by Kovács [105]. The values of the expressions figuring in Table 3.22 ($u_1^+(J)$, $u_3^+(J)$, $C_1(J)$, $C_2(J)$, $C_3(J)$) can be calculated from (2.1.4-9) and (2.1.4-10), by putting $A = 1$ for $^3\Pi$ terms and $A = 2$ for $^3\Delta$ terms. The constants ϱ and σ are each a ratio of two constants given in the paper by Schlapp [193]:

$$\varrho = \frac{B}{\sqrt{2}A} \quad \text{and} \quad \sigma = \frac{D}{E}$$

where A , B and D , E are linear combinations of the components of the electric transition moments, corresponding to the transitions between the states occurring in the linear combinations of the eigenfunctions.

The first confrontation with the $^1\Sigma^- \leftarrow X^3\Sigma^-$ transition of the atmospheric absorption bands of the O_2 molecule as measured by Childs and Mecke [34] was performed by Schlapp [193], with the following result:

Branch	Observed	Calculated
$P(J)$	$J + 1$	$J + 1$
$^PQ(J)$	$J + \frac{1}{2}$	J
$^RQ(J)$	$J + \frac{1}{2}$	$J + 1$
$R(J)$	J	J

Some discrepancy is seen to exist in the case of the two Q branches.

In order to interpret these discrepancies, first Schlapp [194], then Tilford, Vanderlice and Wilkinson [204] generalized those intensity formulas of Table 3.22 which refer to the $^1\Sigma\text{--}^3\Sigma$ transitions, but meanwhile repeated the Schlapp's error in phases. To establish the original formulas in Table 3.22 were calculated the transformation-matrix elements for the $^3\Sigma$ term from (1.5-9) by substituting in it for W_i , the pure case b formulas referring to the $^3\Sigma$ term, i.e. those obtained by putting $D_\Sigma = \varepsilon = \gamma = 0$ in (2.1.4-18), or, which is the same thing, by putting $Y = A = 0$ in (2.1.4-8). If, however, $\varepsilon \gg B$, then the influence of this circumstance upon the form of the formulas cannot any more be neglected in certain cases and, in these cases, the expressions in (2.1.4-19) are to be used to calculate the transformation-matrix elements (although $\gamma = 0$ can be retained). The intensity formulas then modify as shown in Table 3.23 (here already in a corrected form), where for $u^\pm(J)$ see (2.1.4-19c). These formulas reduce to the original formulas in Table 3.22 for $\varepsilon = 0$; on the other hand, for high values of J , the intensities of the branches $^PQ(J)$ and $^RQ(J)$ tend asymptotically to $J + \frac{1}{2}$, in good agreement with experimental results.

* Schlapp, however, made an error in the relative phases ascribed to the two transition moments in the formulas of the $^1\Sigma^\pm\text{--}^3\Sigma^\mp$ transition (Watson [216]), that is the reason why our Tables 3.22 and 3.23 list the $S_{J'J''}^{\pi'\pi''}$ values in a corrected form.

Table 3.23. Modified Form of Intensity Distribution for $^1\Sigma-^3\Sigma$ Transition

$A' - A''$	$A'' - A'$	$^1\Sigma^+ - ^3\Sigma^+$	$A' - A''$	$A'' - A'$	$^1\Sigma^+ - ^3\Sigma^+$
$^0P(J)$	$^S R(J-1)$	$\frac{J[2(J+1) + qu^-(J)]^2}{2(4J(J+1) + u^-(J)^2)}$	$^P Q(J)$	$^R Q(J)$	$\frac{2J(J+1)(2J+1)}{4J(J+1) + u^-(J)^2}$
$^Q R(J)$	$^Q P(J+1)$	$\frac{(J+1)[2J - qu^-(J)]^2}{2(4J(J+1) + u^-(J)^2)}$	$P(J)$	$R(J-1)$	$\frac{J+1}{2}$
$Q(J)$	$Q(J)$	$\frac{2J+1}{2}$	$R(J)$	$P(J+1)$	$\frac{J}{2}$
$^Q P(J)$	$^Q R(J-1)$	$\frac{J[2(J+1) + qu^+(J)]^2}{2(4J(J+1) + u^+(J)^2)}$	$^R Q(J)$	$^P Q(J)$	$\frac{2J(J+1)(2J+1)}{4J(J+1) + u^+(J)^2}$
$^S R(J)$	$^0 P(J+1)$	$\frac{(J+1)[2J - qu^+(J)]^2}{2(4J(J+1) + u^+(J)^2)}$			

In addition to the Σ transition of identical symmetry discussed above, a transition of opposite symmetry was found by Tilford, Vanderslice and Wilkinson [204] for the transition $B'^3\Sigma_u^- \leftarrow X'^1\Sigma_g^+$ in the 7-0 band of the N_2 molecule. Their results are shown in Fig. 3.9. The lines belonging to the branches $^Q P$ and $^Q R$ overlap so that only the sum $^Q P + ^Q R$ could be measured. The calculated intensity sum was found to be nearly twice as great as the observed value. The authors used, however, their own incorrect formulas.

Besides the above ones, Hopfield and Birge [79] and Gerő, Herzberg and Schmid [62] observed transitions of the type $^3\Pi-^1\Sigma$ (Cameron bands) in the CO molecule; Miescher and Wehrli [149, 150] in Ga and in halides, and Mulliken [154] in the halogen molecules. The observed intensities have not, however, been compared so far with the theoretical ones.

Table 3.24 lists the intensities of transitions involving the $^1\Pi$ term, i.e. those of $^1\Pi-^3\Sigma$, $^1\Pi-^1\Sigma$, $^1\Pi-^3\Pi$ (int), $^1\Pi-^3\Delta$ (int). Of these, only the intensities of the transition $^1\Pi-^3\Delta$ (int) have been calculated so far (Kovács [105]). The expressions $u_1^\pm(J)$, $u_3^\pm(J)$, $C_1(J)$, $C_2(J)$, $C_3(J)$, and also the constants λ , ϱ , τ have similar meanings as above. The

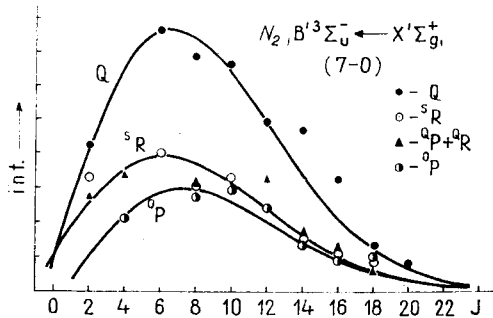


Fig. 3.9 Intensity distribution of the 7-0 band of the transition $B'^3\Sigma_u^- \leftarrow X'^1\Sigma_g^+$ of the N_2 molecule, according to Tilford, Vanderslice, and Wilkinson [204], using (3.1-23).

Table 3.24. Intensity Distribution for ${}^1\Pi$ -Triplet Transitions

$A'-A''$	$A''-A'$	${}^1\Pi'-{}^3\Sigma^{\pm n}$	${}^1\Pi^{\pm}, -{}^3\Pi''(\text{int})$	${}^1\Pi'-{}^3\Pi''(\text{int})$
${}^0P(J)$	${}^SR(J-1)$	$\frac{(J-1)(J+1)}{2(2J+1)} \{1+\lambda\}^2$	$\frac{(J-1)(J+1)}{8JC_3(J)} \{(J+2)u_3^+(J) - J\sigma_{\pm}u_3^-(J) - 4\bar{q}J(J+2)\}^2$	$\frac{(J-1)^2(J+1)(J+2)}{4JC_3(J)} \{\tau u_3^-(J) - 2(J+3)\}^2$
${}^PQ(J)$	${}^RQ(J)$	$\frac{1}{2(J+1)} \{(J+1)+\lambda\}^2$	$\frac{2J+1}{8J(J+1)C_3(J)} \{(J-1)(J+2)u_3^+(J) + J(J+1)\sigma_{\pm}u_3^-(J) + 4\bar{q}J(J+2)\}^2$	$\frac{(J-1)(J+2)(2J+1)}{4J(J+1)C_3(J)} \{\tau u_3^-(J) + 2(J-1)(J+3)\}^2$
${}^Q_R(J)$	${}^QP(J+1)$	$\frac{J+2}{2(J+1)(2J+1)} \{(J+1)-\lambda J\}^2$	$\frac{J(J+2)}{8(J+1)C_3(J)} \{(J-1)u_3^+(J) - (J+1)\sigma_{\pm}u_3^-(J) + 4\bar{q}J(J+2)\}^2$	$\frac{(J-1)J}{4(J+1)C_3(J)} \{(J+2)\tau u_3^-(J) + 2(J-1)(J+3)\}^2$
${}^P(J)$	${}^R(J-1)$	$\frac{(J-1)(J+1)}{2J} \lambda^2$	$\frac{(J-1)(J+1)}{JC_2(J)} \{(J+2) + J\sigma_{\pm} + \bar{q}(Y-2)\}^2$	$\frac{2(J+1)(J+2)}{JC_2(J)} \{\tau(J-1) - (Y-2)\}^2$
${}^Q(J)$	${}^Q(J)$	$\frac{2J+1}{2J(J+1)} \lambda^2$	$\frac{2J+1}{J(J+1)C_2(J)} \{(J-1)(J+2) - J(J+1)\sigma_{\pm} - \bar{q}(Y-2)\}^2$	$\frac{2(J-1)(J+2)(2J+1)}{J(J+1)C_2(J)} \{\tau + (Y-2)\}^2$
${}^R(J)$	${}^P(J+1)$	$\frac{J(J+2)}{2(J+1)} \lambda^2$	$\frac{J(J+2)}{(J+1)C_2(J)} \{(J-1) + (J+1)\sigma_{\pm} - \bar{q}(Y-2)\}^2$	$\frac{2(J-1)J}{(J+1)C_2(J)} \{\tau(J+2) + (Y-2)\}^2$
${}^QP(J)$	${}^QR(J-1)$	$\frac{J-1}{2J(2J+1)} \{J-\lambda(J+1)\}^2$	$\frac{(J-1)(J+1)}{8JC_1(J)} \{(J+2)u_1^-(J) - J\sigma_{\pm}u_1^+(J) + 4\bar{q}(J-1)(J+1)\}^2$	$\frac{(J+1)(J+2)}{4JC_1(J)} \{(J-1)\tau u_1^-(J) + 2(J-2)(J+2)\}^2$
${}^RQ(J)$	${}^PQ(J)$	$\frac{1}{2J} \{J-\lambda\}^2$	$\frac{2J+1}{8J(J+1)C_1(J)} \{(J-1)(J+2)u_1^-(J) + J(J+1)\sigma_{\pm}u_1^+(J) - 4\bar{q}(J-1)(J+1)\}^2$	$\frac{(J-1)(J+2)(2J+1)}{4J(J+1)C_1(J)} \{\tau u_1^-(J) - 2(J-2)(J+2)\}^2$
${}^SR(J)$	${}^OP(J+1)$	$\frac{J(J+2)}{2(2J+1)} \{1+\lambda\}^2$	$\frac{J(J+2)}{8(J+1)C_1(J)} \{(J-1)u_1^-(J) - (J+1)\sigma_{\pm}u_1^+(J) - 4\bar{q}(J-1)(J+1)\}^2$	$\frac{(J-1)J(J+2)^2}{4(J+1)C_1(J)} \{\tau u_1^-(J) - 2(J-2)\}^2$

Table 3.25. Intensity Distribution for ${}^1A'$ -Triplet Transitions

$A' - A''$	$A'' - A'$	${}^1A' - {}^3\Sigma''$	${}^1A - {}^3\Pi''(\text{int})$	${}^1A' - {}^3A''(\text{int})$
${}^0P(J)$	${}^5R(J-1)$	$\frac{(J-2)(J-1)}{4(2J+1)}$	$\frac{(J-2)(J-1)(J+2)^2}{4JC_3(J)} \{ \lambda u_3^+(J) + 2J \}^2$	$\frac{(J-2)(J+2)}{8JC_3(J)} \{ (J+3)u_3^+(J) - (J-1)\sigma u_3^-(J) - 4\varrho(J-1)(J+3) \}^2$
${}^PQ(J)$	${}^RQ(J)$	$\frac{(J-1)(J+2)}{4(J+1)}$	$\frac{(J-1)(J+2)(2J+1)}{J(J+1)C_3(J)} \{ \lambda u_3^+(J) + J(J+2) \}^2$	$\frac{2J+1}{8J(J+1)C_3(J)} \{ (J-2)(J+3)u_3^+(J) + (J-1)(J+2)\sigma u_3^-(J) + 8\varrho(J-1)(J+3) \}^2$
${}^QR(J)$	${}^QP(J+1)$	$\frac{J(J+2)(J+3)}{4(J+1)(2J+1)}$	$\frac{(J+2)(J+3)}{4(J+1)C_3(J)} \{ (J-1)\lambda u_3^+(J) - 2J(J+2) \}^2$	$\frac{(J-1)(J+3)}{8(J+1)C_3(J)} \{ (J-2)u_3^+(J) - (J+2)\sigma u_3^-(J) + 4\varrho(J-1)(J+3) \}^2$
${}^P(J)$	${}^R(J-1)$	$\frac{(J-2)(J-1)}{4J}$	$\frac{(J-2)(J-1)}{2JC_2(J)} \{ 2(J+2)\lambda - (Y-2) \}^2$	$\frac{(J-2)(J+2)}{JC_2(J)} \{ (J+3) + (J-1)\sigma + 2\varrho(Y-2) \}^2$
${}^Q(J)$	${}^Q(J)$	$\frac{(J-1)(J+2)(2J+1)}{4J(J+1)}$	$\frac{(J-1)(J+2)(2J+1)}{2J(J+1)C_2(J)} \{ 4\lambda - (Y-2) \}^2$	$\frac{(2J+1)}{J(J+1)C_2(J)} \{ (J-2)(J+3) - (J-1)(J+2)\sigma - 4\varrho(Y-2) \}^2$
${}^R(J)$	${}^P(J+1)$	$\frac{(J+2)(J+3)}{4(J+1)}$	$\frac{(J+2)(J+3)}{2(J+1)C_2(J)} \{ 2(J-1)\lambda + (Y-2) \}^2$	$\frac{(J-1)(J+3)}{(J+1)C_2(J)} \{ (J-2) + (J+2)\sigma - 2\varrho(Y-2) \}^2$
${}^QP(J)$	${}^QR(J-1)$	$\frac{(J-2)(J-1)(J+1)}{4J(2J+1)}$	$\frac{(J-2)(J-1)}{4JC_1(J)} \{ (J+2)\lambda u_1^-(J) - 2(J-1)(J+1) \}^2$	$\frac{(J-2)(J+2)}{8JC_1(J)} \{ (J+3)u_1^-(J) - (J-1)\sigma u_1^+(J) + 4\varrho(J-2)(J+2) \}^2$
${}^RQ(J)$	${}^PQ(J)$	$\frac{(J-1)(J+2)}{4J}$	$\frac{(J-1)(J+2)(2J+1)}{J(J+1)C_1(J)} \{ \lambda u_1^-(J) - (J-1)(J+1) \}^2$	$\frac{2J+1}{8J(J+1)C_1(J)} \{ (J-2)(J+3)u_1^-(J) + (J-1)(J+2)\sigma u_1^+(J) - 8\varrho(J-2)(J+2) \}^2$
${}^SR(J)$	${}^0P(J+1)$	$\frac{(J+2)(J+3)}{4(2J+1)}$	$\frac{(J-1)^2(J+2)(J+3)}{4(J+1)C_1(J)} \{ \lambda u_1^-(J) + 2(J+1) \}^2$	$\frac{(J-1)(J+3)}{8(J+1)C_1(J)} \{ (J-2)u_1^-(J) - (J+2)\sigma u_1^+(J) - 4\varrho(J-2)(J+2) \}^2$

symbol σ_{\pm} denotes the sum (or difference) of two such constants; in view of the different symmetry of the two components of the Δ -type doublet of the ${}^1\Pi$ term, for ${}^1\Pi^{+}$ the sum is to be taken in the P and R branches, and the difference in the Q branches (for ${}^1\Pi^{-}$, the opposite holds).

If we reduce the above general formulas of the transition ${}^1\Pi-{}^3\Pi$ by the substitutions $Y \rightarrow \infty$ and $Y = 0$ to the simpler formulas of the transitions ${}^1\Pi-{}^3\Pi(a)$ and ${}^1\Pi-{}^3\Pi(b)$, respectively, we obtain expressions identical with those derived by Chiu [36] starting from the assumption of *magnetic di-pole* radiation. Chiu also gave intensity-distribution formulas of these transitions for *electric quadrupole* radiation; these differ from the previous ones, and, in addition, permit some transitions 'forbidden' in the general case.

Table 3.25 lists the transitions involving the term ${}^1\Delta$, i.e. ${}^1\Delta-{}^3\Sigma$, ${}^1\Delta-{}^3\Pi(\text{int})$, ${}^1\Delta-{}^3\Delta(\text{int})$ are found. Of these, the case of the transitions ${}^1\Delta-{}^3\Sigma$ has been discussed by van Vleck [213]; the others are given here for the first time. The notation used in Table 3.24 is similar to that used previously.

Van Vleck has also shown that, in the case of the transitions ${}^1\Delta-{}^3\Sigma$, *magnetic di-pole* radiation apart from symmetry characters leads to the same result as the formulas based on the spin-orbit interaction and given here.

3.3.2. Doublet-Quartet Transitions

Experiment has shown that, in addition to singlet-triplet transitions, intercombination transitions of higher multiplicity, namely doublet-quartet transitions also occur. The intensities of these transitions can also be derived by the general procedure described in 3.3. In the following, we shall restrict the application of that procedure to the terms Σ and Π ; even, in the case of the ${}^4\Pi$ terms, only the formulas for the transitions involving the terms ${}^4\Pi(a)$ and ${}^4\Pi(b)$ will be given, in order to avoid the extremely complicated expressions connected with ${}^4\Pi(\text{int})$. Accordingly, we shall list, in Table 3.26, from among the formulas of the transitions involving ${}^2\Sigma$, those for ${}^2\Sigma^{\pm}-{}^4\Sigma^{\pm}$, ${}^2\Sigma^{\pm}-{}^4\Sigma^{\mp}$, according to Budó and Kovács [24] (but here in a corrected form), in Tables 3.27 and 3.28, those for ${}^2\Sigma-{}^4\Pi(a)$, and ${}^2\Sigma-{}^4\Pi(b)$ according to Kovács and Budó [121]. The constants occurring in the tables have similar meaning as previously. It should be noted that in the double-sign formulas in Table 3.27 the upper sign refers to the left-hand branches, and *vice versa*. In the same table, if an inverted ${}^4\Pi$ term turns up, the second suffixes in the first and fourth columns and the first suffixes in the second and fifth columns are to be changed according to the pattern $1 \rightarrow 4$, $2 \rightarrow 3$, etc.

Tables 3.29, 3.30 and 3.31 list the transitions involving the ${}^2\Pi$ terms, namely ${}^2\Pi(\text{int})-{}^4\Sigma$, ${}^2\Pi(\text{int})-{}^4\Pi(a)$ and ${}^2\Pi(\text{int})-{}^4\Pi(b)$. The formulas relating to the intermediate ${}^2\Pi$ term are published here for the first time, whereas the limiting-case formulas which can be obtained from these by simple substitutions were first given by the above authors in [24] and [121]. For the notations $u^{\pm}(J)$, $C^{\pm}(J)$ see (2.1.3-6). Of the double signs in the formulas, the upper one always refers to the upper branch of the closely-

Table 3.26. Intensity Distribution for ${}^2\Sigma-{}^4\Sigma$ Transitions

$A'-A''$	$A''-A'$	${}^2\Sigma^+-{}^4\Sigma^+$	${}^2\Sigma^+-{}^4\Sigma^+$
$Q_{P_{21}(J)}$	$Q_{R_{12}(J-1)}$	0	$\frac{3(J+1/2)}{8J^2} [\sqrt{2}Q(J-1/2)+(J+1/2)]^2$
$R_{Q_{21}(J)}$	$P_{Q_{12}(J)}$	$\frac{3(J-1/2)(J+1/2)(J+1)}{4J^2}$	0
$S_{R_{21}(J)}$	$O_{P_{12}(J+1)}$	0	$\frac{3(J-1/2)(J+1/2)(J+3/2)}{8J(J+1)} [\sqrt{2}Q-1]^2$
$P_2(J)$	$R_2(J-1)$	$\frac{(J+1/2)(J+1)}{2J}$	0
$Q_2(J)$	$Q_2(J)$	0	$\frac{(J-1/2)(J+1/2)}{16J(J+1)^2} [\sqrt{2}Q-(4J+5)]^2$
$R_2(J)$	$P_2(J+1)$	$\frac{(J-1/2)(J+1/2)(J+3/2)}{2(J+1)^2}$	0
$O_{P_{23}(J)}$	$S_{R_{22}(J-1)}$	0	$\frac{(J-1/2)(J+1/2)(J+3/2)}{8J^2} [\sqrt{2}Q-1]^2$
$P_{Q_{23}(J)}$	$R_{Q_{32}(J)}$	$\frac{(J+1/2)(J+3/2)(J-1)^2}{4J^2(J+1)}$	0
$Q_{R_{23}(J)}$	$Q_{P_{32}(J+1)}$	0	$\frac{J+1/2}{8J(J+1)} [\sqrt{2}Q(J+3/2)+(J-3/2)]^2$
$N_{P_{24}(J)}$	$T_{R_{42}(J-1)}$	0	0
$O_{Q_{24}(J)}$	$S_{Q_{42}(J)}$	0	$\frac{3(J+1/2)(J+3/2)}{16J(J+1)^2} [\sqrt{2}Q-1]^2$
$P_{R_{24}(J)}$	$R_{P_{42}(J+1)}$	$\frac{3(J+1/2)}{8(J+1)^2}$	0
$R_{P_{31}(J)}$	$P_{R_{13}(J-1)}$	$\frac{3(J+1/2)}{8J^2}$	0
$S_{Q_{31}(J)}$	$O_{Q_{13}(J)}$	0	$\frac{3(J-1/2)(J+1/2)}{16J^2(J+1)} [\sqrt{2}Q-1]^2$
$T_{R_{31}(J)}$	$N_{P_{13}(J+1)}$	0	0
$Q_{P_{32}(J)}$	$Q_{R_{23}(J-1)}$	0	$\frac{J+1/2}{8J(J+1)} [\sqrt{2}Q(J-1/2)+(J+5/2)]^2$
$R_{Q_{32}(J)}$	$P_{Q_{23}(J)}$	$\frac{(J-1/2)(J+1/2)(J+2)^2}{4J(J+1)^2}$	0
$S_{R_{32}(J)}$	$O_{P_{23}(J+1)}$	0	$\frac{(J-1/2)(J+1/2)(J+3/2)}{8(J+1)^2} [\sqrt{2}Q-1]^2$

Table 3.26 (continued)

$A' - A''$	$A'' - A'$	${}^2\Sigma^+ - {}^4\Sigma^+$	${}^2\Sigma^+ - {}^4\Sigma^+$
$P_3(J)$	$R_3(J-1)$	$\frac{(J-1/2)(J+1/2)(J+3/2)}{2J^2}$	0
$Q_3(J)$	$Q_3(J)$	0	$\frac{(J+1/2)(J+3/2)}{16J^2(J+1)} [V\bar{2}\varrho + (4J-1)]^2$
$R_3(J)$	$P_3(J+1)$	$\frac{(J+1/2)J}{2(J+1)}$	0
${}^oP_{34}(J)$	${}^SR_{43}(J-1)$	0	$\frac{3(J-1/2)(J+1/2)(J+3/2)}{8J(J+1)} [V\bar{2}\varrho - 1]^2$
${}^PQ_{34}(J)$	${}^RQ_{43}(J)$	$\frac{3(J+1/2)(J+3/2)J}{4(J+1)^2}$	0
${}^Q R_{34}(J)$	${}^Q P_{43}(J+1)$	0	$\frac{3(J+1/2)}{8(J+1)^2} [V\bar{2}\varrho(J+3/2) + (J+1/2)]^2$

Table 3.27. Intensity Distribution for ${}^2\Sigma - {}^4\Pi$ Transitions

$A' - A''$	$A'' - A'$	${}^2\Sigma' - {}^4\Pi(a)''$	$A' - A''$	$A'' - A'$
${}^Q P_{21}(J)$	${}^Q R_{12}(J-1)$	$\frac{3(J-1/2)(J+1/2)}{4J} \sigma^2$	${}^R P_{31}(J)$	${}^P R_{13}(J-1)$
${}^R Q_{21}(J)$	${}^P Q_{12}(J)$	$\frac{3(J+1/2)}{8J(J+1)} \sigma^2$	${}^S Q_{31}(J)$	${}^O Q_{13}(J)$
${}^S R_{21}(J)$	${}^O P_{12}(J+1)$	$\frac{3(J+1/2)(J+3/2)}{4(J+1)} \sigma^2$	${}^T R_{31}(J)$	${}^N P_{13}(J+1)$
$P_2(J)$	$R_2(J-1)$	$\frac{(J-1/2)(J+3/2)}{4J} [\sigma \pm 1]^2$	${}^Q P_{32}(J)$	${}^Q R_{23}(J-1)$
$Q_2(J)$	$Q_2(J)$	$\frac{(J+1/2)}{2J(J+1)} \left[\frac{\sigma}{2} \mp (J+1/2) \right]^2$	${}^R Q_{32}(J)$	${}^P Q_{23}(J)$
$R_2(J)$	$P_2(J+1)$	$\frac{(J+1/2)(J+3/2)}{4(J+1)} [\sigma \mp 1]^2$	${}^S R_{32}(J)$	${}^O P_{23}(J+1)$
${}^O P_{23}(J)$	${}^S R_{32}(J-1)$	$\frac{(J+1/2)(J+3/2)}{4J}$	$P_3(J)$	$R_3(J-1)$
${}^P Q_{23}(J)$	${}^R Q_{32}(J)$	$\frac{(J-1/2)(J+1/2)(J+3/2)}{2J(J+1)}$	$Q_3(J)$	$Q_3(J)$
${}^Q R_{23}(J)$	${}^Q P_{32}(J+1)$	$\frac{(J-1/2)(J+1/2)}{4(J+1)}$	$R_3(J)$	$P_3(J+1)$

Table 3.27 (continued)

$A'-A''$	$A''-A'$	${}^2\Sigma'-{}^4\Pi(a)''$	$A'-A''$	$A''-A'$
${}^N P_{24}(J)$	${}^T R_{42}(J-1)$	0	${}^O P_{34}(J)$	${}^S R_{43}(J-1)$
${}^O Q_{24}(J)$	${}^S Q_{42}(J)$	0	${}^P Q_{34}(J)$	${}^R Q_{43}(J)$
${}^P R_{24}(J)$	${}^R P_{42}(J+1)$	0	${}^Q R_{34}(J)$	${}^Q P_{43}(J+1)$

Table 3.28. Intensity Distribution for ${}^2\Sigma-{}^4\Pi$ Transitions

$A'-A''$	$A''-A'$	${}^2\Sigma'-{}^4\Pi(b)''$
${}^O P_{21}(J)$	${}^Q R_{12}(J-1)$	$\frac{3(J-\frac{3}{2})(J+\frac{1}{2})}{8J^2(J-\frac{1}{2})} [\sigma(J-\frac{1}{2}) + (J+\frac{1}{2})]^2$
${}^R Q_{21}(J)$	${}^P Q_{12}(J)$	$\frac{3(J-\frac{3}{2})(J+\frac{1}{2})}{16J^2(J+1)} [\sigma - 2(J+1)]^2$
${}^S R_{21}(J)$	${}^O P_{12}(J+1)$	$\frac{3(J-\frac{3}{2})(J+\frac{1}{2})(J+\frac{3}{2})}{8J(J+1)} [\sigma - 1]^2$
${}^P_2(J)$	${}^R_2(J-1)$	$\frac{(J+1)}{2J(J-\frac{1}{2})} [\sigma(J-\frac{1}{2}) + 1]^2$
${}^Q_2(J)$	${}^Q_2(J)$	$\frac{1}{16J(J+1)^2} [2\sigma(J+1) - (5J+\frac{13}{2})]^2$
${}^R_2(J)$	${}^P_2(J+1)$	$\frac{J+\frac{3}{2}}{3(J+1)^2} [2\sigma(J+1) - 3]^2$
${}^O P_{23}(J)$	${}^S R_{32}(J-1)$	$\frac{(J-\frac{1}{2})(J+\frac{3}{2})^2}{8J^2} [\sigma - 1]^2$
${}^P Q_{23}(J)$	${}^R Q_{32}(J)$	$\frac{[\sigma(J+\frac{3}{2}) + (J-\frac{1}{2})(J+\frac{9}{2}) + (J-\frac{3}{2})(J+\frac{1}{2})]^2}{16J^2(J+1)}$
${}^Q R_{23}(J)$	${}^Q P_{32}(J+1)$	$\frac{[2\sigma(J+\frac{3}{2})^2 + (J-\frac{1}{2})(J+\frac{9}{2}) + (J-\frac{3}{2})(J+\frac{3}{2})]^2}{32J(J+1)(J+\frac{3}{2})}$
${}^N P_{24}(J)$	${}^T R_{42}(J-1)$	0
${}^O Q_{24}(J)$	${}^S Q_{42}(J)$	$\frac{3(J+\frac{1}{2})(J+\frac{5}{2})}{16J(J+1)^2}$
${}^P R_{24}(J)$	${}^R P_{42}(J+1)$	$\frac{3(J+\frac{1}{2})(J+\frac{5}{2})}{8(J+1)^2(J+\frac{3}{2})}$

Table 3.28 (continued)

$A' - A''$	$A'' - A'$	${}^2\Sigma' - {}^4\Pi(b)''$
${}^R P_{31}(J)$	${}^P R_{13}(J - 1)$	$\frac{3(J - \frac{3}{2})(J + \frac{1}{2})}{8J^2(J - \frac{1}{2})}$
${}^S Q_{31}(J)$	${}^O Q_{13}(J)$	$\frac{3(J - \frac{3}{2})(J + \frac{1}{2})}{16J^2(J + 1)}$
${}^T R_{31}(J)$	${}^N P_{13}(J + 1)$	0
${}^Q P_{32}(J)$	${}^Q R_{23}(J - 1)$	$\frac{[2\sigma(J - \frac{1}{2})^2 + (J - \frac{7}{2})(J + \frac{3}{2}) + (J - \frac{1}{2})(J + \frac{5}{2})]^2}{32J(J + 1)(J - \frac{1}{2})}$
${}^R Q_{32}(J)$	${}^P Q_{23}(J)$	$\frac{[\sigma(J - \frac{1}{2}) - (J - \frac{7}{2})(J + \frac{3}{2}) - (J + \frac{1}{2})(J + \frac{5}{2})]^2}{16J(J + 1)^2}$
${}^S R_{32}(J)$	${}^O P_{23}(J + 1)$	$\frac{(J - \frac{1}{2})^2(J + \frac{3}{2})}{8(J + 1)^2} [\sigma - 1]^2$
${}^P P_3(J)$	${}^R R_3(J - 1)$	$\frac{(J - \frac{1}{2})}{8J^2} [2\sigma J + 3]^2$
${}^Q Q_3(J)$	${}^Q Q_3(J)$	$\frac{1}{16J^2(J + 1)} [2\sigma J - (5J - \frac{3}{2})]^2$
${}^R R_3(J)$	${}^P P_3(J + 1)$	$\frac{J}{2(J + 1)(J + \frac{3}{2})} [\sigma(J + \frac{3}{2}) - 1]^2$
${}^O P_{34}(J)$	${}^S R_{43}(J - 1)$	$\frac{3(J - \frac{1}{2})(J + \frac{1}{2})(J + \frac{5}{2})}{8J(J + 1)} [\sigma - 1]^2$
${}^P Q_{34}(J)$	${}^R Q_{43}(J)$	$\frac{3(J + \frac{1}{2})(J + \frac{5}{2})}{16J(J + 1)^2} [\sigma + 2J]^2$
${}^Q R_{34}(J)$	${}^Q P_{43}(J + 1)$	$\frac{3(J + \frac{1}{2})(J + \frac{5}{2})}{8(J + 1)^2(J + \frac{3}{2})} [\sigma(J + \frac{3}{2}) + (J + \frac{1}{2})]^2$

spaced pair of branches, and *vice versa*. Furthermore, the constant v in Tables 3.30 and 3.31 is of *opposite sign* for the two components of the A -type doublet. In Table 3.30 if an inverted ${}^4\Pi$ term turns up the second suffixes in the first column and the first suffixes in the second column are to be changed according to the pattern $1 \rightarrow 4, 2 \rightarrow 3$, etc. If the ${}^2\Pi$ term is an inverted one, then the sign of Y is to be changed in $u^\pm(J)$ and $C^\pm(J)$.

In the field of experimental application, it was Åkerlind who used the above formulas to estimate the relative intensities of the transitions ${}^2\Sigma - {}^4\Sigma$ observed in the LaO [8] and ScO [7] molecules; he found a good agreement between the estimated and observed values.

Table 3.29. Intensity Distribution for ${}^2\Pi-{}^4\Sigma$ Transitions

$A'-A''$	$A''-A'$	${}^2\Pi'(\text{int})-{}^4\Sigma''$
${}^Q P_{21}(J)$ ${}^R P_{31}(J)$	${}^Q R_{12}(J-1)$ ${}^P R_{13}(J-1)$	$\frac{3(J - 3/2)}{32J^2 C^\mp(J-1)} \{ \tau(J - 1/2) [u^\mp(J-1) \pm 2(J + 1/2)]$ $+ (J + 3/2)u^\mp(J-1) \pm 2(J - 1/2)(J + 1/2) \}^2$
${}^R Q_{21}(J)$ ${}^S Q_{31}(J)$	${}^P Q_{12}(J)$ ${}^O Q_{13}(J)$	$\frac{3(J+1/2)(J+3/2)}{64J^2(J+1)C^\mp(J)} \{ 2\tau(J - 1/2) [u^\mp(J) \pm 2(J + 1/2)] + 3u^\mp(J)$ $\pm 2(J - 1/2) \}^2$
${}^S R_{21}(J)$ ${}^T R_{31}(J)$	${}^O P_{12}(J+1)$ ${}^N P_{13}(J+1)$	$\frac{3(J - 1/2)(J+3/2)(J+5/2)}{32J(J+1)C^\mp(J+1)} \{ (\tau - 1) [u^\mp(J+1) \pm 2(J + 1/2)] \}^2$
${}^P_2(J)$ ${}^Q P_{32}(J)$	${}^R_2(J-1)$ ${}^Q R_{23}(J-1)$	$\frac{J - 3/2}{32J(J+1)C^\mp(J-1)} \{ \tau(J-1/2) [u^\mp(J-1) \mp 2(J+1/2)]$ $+ 3(J+3/2)u^\mp(J-1) \pm 2(J - 1/2)(J + 1/2) \}^2$
${}^Q_2(J)$ ${}^R Q_{32}(J)$	${}^Q_2(J)$ ${}^P Q_{23}(J)$	$\frac{(J+1/2)(J+3/2)}{64J(J+1)^2 C^\mp(J)} \{ 2\tau(J - 1/2) [u^\mp(J) \mp 2(J + 1/2)] + 9u^\mp(J)$ $\pm 2(J - 1/2) \}^2$
${}^R_2(J)$ ${}^S R_{32}(J)$	${}^P_2(J+1)$ ${}^O P_{23}(J+1)$	$\frac{(J-1/2)(J+3/2)(J+5/2)}{32(J+1)^2 C^\mp(J+1)} \{ \tau[u^\mp(J+1) \mp 2(J + 1/2)]$ $- 3u^\mp(J+1) \mp 2(J + 1/2) \}^2$
${}^O P_{23}(J)$ ${}^P_3(J)$	${}^S R_{33}(J-1)$ ${}^R_3(J-1)$	$\frac{(J-3/2)(J-1/2)(J+5/2)}{32J^2 C^\mp(J-1)} \{ \tau[u^\mp(J-1) \pm 2(J+1/2)] - 3u^\mp(J-1)$ $\pm 2(J + 1/2) \}^2$
${}^P Q_{23}(J)$ ${}^Q_3(J)$	${}^R Q_{32}(J)$ ${}^Q_3(J)$	$\frac{(J - 1/2)(J+1/2)}{64J^2(J+1)C^\mp(J)} \{ 2\tau(J + 3/2) [u^\mp(J) \pm 2(J + 1/2)] - 9u^\mp(J)$ $\pm 2(J + 3/2) \}^2$
${}^Q R_{23}(J)$ ${}^R_3(J)$	${}^Q P_{32}(J+1)$ ${}^P_3(J+1)$	$\frac{J + 5/2}{32J(J+1)C^\mp(J+1)} \{ \tau(J + 3/2) [u^\mp(J+1) \pm 2(J + 1/2)]$ $+ 3(J-1/2)u^\mp(J+1) \mp 2(J+1/2)(J+3/2) \}^2$
${}^N P_{24}(J)$ ${}^O P_{34}(J)$	${}^T R_{42}(J-1)$ ${}^S R_{43}(J-1)$	$\frac{3(J-3/2)(J-1/2)(J+3/2)}{32J(J+1)C^\mp(J)} \{ (\tau - 1) [u^\mp(J-1) \mp 2(J + 1/2)] \}^2$
${}^O Q_{24}(J)$ ${}^P Q_{34}(J)$	${}^S Q_{42}(J)$ ${}^R Q_{43}(J)$	$\frac{3(J-1/2)(J+1/2)}{64J(J+1)^2 C^\mp(J)} \{ 2\tau(J + 3/2) [u^\mp(J) \mp 2(J + 1/2)] - 3u^\mp(J)$ $\pm 2(J + 3/2) \}^2$
${}^P R_{24}(J)$ ${}^Q R_{34}(J)$	${}^R P_{42}(J+1)$ ${}^Q P_{43}(J+1)$	$\frac{3(J + 5/2)}{32(J+1)^2 C^\mp(J+1)} \{ \tau(J + 3/2) [u^\mp(J+1) \mp 2(J + 1/2)]$ $+ (J - 1/2)u^\mp(J+1) \mp 2(J + 1/2)(J+3/2) \}^2$

Kleman and Werhagen [92] found ${}^4\Sigma-{}^2\Pi$ transitions in the GeH molecule; comparing the estimated relative intensities of the branches with the observed ones, they found a good agreement. Åkerlind applied the formulas also to the ${}^2\Pi-{}^4\Sigma$ transitions of the LaO [8] and ScO [7] molecules, but he found the relative intensities of the branches to deviate from theory

Table 3.30. Intensity Distribution for ${}^2\Pi-{}^4\Pi$ Transitions

$A'-A''$	$A''-A'$	${}^2\Pi'(\text{int})-{}^4\Pi(a)''$
${}^Q P_{21}(J)$ ${}^R P_{31}(J)$	${}^Q R_{12}(J-1)$ ${}^P R_{13}(J-1)$	$\frac{3(J-\frac{3}{2})(J-\frac{1}{2})}{8JC^\mp(J-1)} \{vu^\mp(J-1) \pm 2(J+\frac{1}{2})\}^2$
${}^R Q_{21}(J)$ ${}^S Q_{31}(J)$	${}^P Q_{12}(J)$ ${}^O Q_{13}(J)$	$\frac{3(J-\frac{1}{2})(J+\frac{1}{2})(J+\frac{3}{2})}{4J(J+1)C^\mp(J)} \{vu^\mp(J) \pm 2(J+\frac{1}{2})\}^2$
${}^S R_{21}(J)$ ${}^T R_{31}(J)$	${}^O P_{12}(J+1)$ ${}^N P_{13}(J+1)$	$\frac{3(J+\frac{3}{2})(J+\frac{5}{2})}{8(J+1)C^\mp(J+1)} \{vu^\mp(J+1) \pm 2(J+\frac{1}{2})\}^2$
$P_2(J)$ ${}^Q P_{32}(J)$	$R_2(J-1)$ ${}^Q R_{23}(J-1)$	$\frac{(J-\frac{3}{2})(J-\frac{1}{2})}{8JC^\mp(J-1)} \{u^\mp(J-1) \pm 2(v+\lambda)(J+\frac{1}{2})\}^2$
$Q_2(J)$ ${}^R Q_{32}(J)$	$Q_2(J)$ ${}^P Q_{23}(J)$	$\frac{(J-\frac{1}{2})(J+\frac{1}{2})(J+\frac{3}{2})}{4J(J+1)C^\mp(J)} \{u^\mp(J) \pm 2v(J+\frac{1}{2}) \pm \lambda\}^2$
$R_2(J)$ ${}^S R_{32}(J)$	$P_2(J+1)$ ${}^O P_{23}(J+1)$	$\frac{(J+\frac{3}{2})(J+\frac{5}{2})}{8(J+1)C^\mp(J+1)} \{u^\mp(J+1) \pm 2(v-\lambda)(J+\frac{1}{2})\}^2$
${}^O P_{23}(J)$ $P_3(J)$	${}^S R_{32}(J-1)$ $R_3(J-1)$	$\frac{(J-\frac{3}{2})(J+\frac{3}{2})}{8JC^\mp(J-1)} \{\lambda u^\mp(J-1) \pm 2\omega(J+\frac{1}{2})\}^2$
${}^P Q_{23}(J)$ $Q_3(J)$	${}^R Q_{32}(J)$ $Q_3(J)$	$\frac{J+\frac{1}{2}}{16J(J+1)C^\mp(J)} \{3\lambda u^\mp(J) \mp 4\omega(J-\frac{1}{2})(J+\frac{3}{2})\}^2$
${}^Q R_{23}(J)$ $R_3(J)$	${}^Q P_{32}(J+1)$ $P_3(J+1)$	$\frac{(J-\frac{1}{2})(J+\frac{5}{2})}{8(J+1)C^\mp(J+1)} \{\lambda u^\mp(J+1) \mp 2\omega(J+\frac{1}{2})\}^2$
${}^N P_{24}(J)$ ${}^O P_{34}(J)$	${}^T R_{24}(J-1)$ ${}^S R_{43}(J-1)$	$\frac{3(J+\frac{3}{2})(J+\frac{5}{2})}{8JC^\mp(J-1)} \{\omega u^\mp(J-1)\}^2$
${}^O Q_{24}(J)$ ${}^P Q_{34}(J)$	${}^S Q_{42}(J)$ ${}^R Q_{43}(J)$	$\frac{3(J-\frac{3}{2})(J+\frac{1}{2})(J+\frac{5}{2})}{4J(J+1)C^\mp(J)} \{\omega u^\mp(J)\}^2$
${}^P R_{24}(J)$ ${}^Q R_{34}(J)$	${}^R P_{42}(J+1)$ ${}^Q P_{43}(J+1)$	$\frac{3(J-\frac{3}{2})(J-\frac{1}{2})}{8(J+1)C^\mp(J+1)} \{\omega u^\mp(J+1)\}^2$

for two branches, namely ${}^Q R_{23}$ and P_2 . Since in the formulas he used the ${}^2\Pi$ term was in the case a form, it is possible that the intermediate-case formulas given here for the ${}^2\Pi$ term would give a better approximation of the observed values.

Finally, the formulas for the transitions ${}^4\Pi-{}^2\Pi$ were applied by Frosch and Robinson [53] to the $a{}^4\Pi-X{}^2\Pi$ transitions of the NO molecule.

Among the intercombination transitions of higher multiplicity, the formulas for the transitions ${}^2\Sigma^+-{}^6\Sigma^+$ and ${}^2\Sigma^+-{}^6\Sigma^+$ have been derived by Kovács and Scari [126]; these, however, necessitate taking into account the second-order terms neglected so far and thus give much lower intensities. No experimental verification of these has been performed until now.

Table 3.31. Intensity Distribution for ${}^2\Pi-{}^4\Pi$ Transitions

$\Lambda'-\Lambda''$	$\Lambda'-\Lambda'$	${}^2\Pi'(\text{int})-{}^4\Pi(b)''$
$Q P_{21}(J)$ $R P_{31}(J)$	$Q R_{12}(J-1)$ $P R_{13}(J-1)$	$\frac{3}{64J^2(J-\frac{1}{2})O^{\mp}(J-1)} \{(1+v)(J-\frac{3}{2})(J-\frac{1}{2})[u^{\mp}(J-1) \pm 2(J+\frac{1}{2})] + \omega(J+\frac{3}{2})[(J+\frac{5}{2}) \pm 2(J-\frac{1}{2})] \}^2$ $\times u^{\mp}(J-1) \pm 2(J-\frac{3}{2})(J+\frac{1}{2}) + \lambda(J-\frac{3}{2})[(J+\frac{3}{2})u^{\mp}(J-1) \pm 2(J-\frac{1}{2})(J+\frac{1}{2})]^2$
$R Q_{21}(J)$ $S Q_{31}(J)$	$P Q_{12}(J)$ $O Q_{13}(J)$	$\frac{3(J-\frac{3}{2})(J+\frac{1}{2})(J+\frac{3}{2})}{32J^2(J+1)(J-\frac{1}{2})O^{\mp}(J)} \{(1+v)(J-\frac{1}{2})[u^{\mp}(J) \pm 2(J+\frac{1}{2})] - \omega[(J+\frac{5}{2})u^{\mp}(J) \pm 2(J-\frac{1}{2}) \pm 2(J-\frac{1}{2})] \}^2$ $\times (J+\frac{3}{2}) + \lambda[\frac{3}{2}u^{\mp}(J) \pm (J-\frac{1}{2})]^2$
$S R_{21}(J)$ $T R_{31}(J)$	$O P_{12}(J+1)$ $N P_{13}(J+1)$	$\frac{3(J-\frac{3}{2})(J+\frac{3}{2})(J+\frac{5}{2})}{64J(J+1)O^{\mp}(J+1)} \{(1+v+\omega-\lambda)[u^{\mp}(J+1) \pm 2(J+\frac{1}{2})]\}^2$
$P_{21}(J)$ $Q P_{32}(J)$	$R_{21}(J-1)$ $Q R_{23}(J-1)$	$\frac{J-\frac{3}{2}}{64J(J+1)(J-\frac{1}{2})(J+\frac{1}{2})O^{\mp}(J-1)} \{(J-\frac{1}{2})(J+\frac{5}{2})u^{\mp}(J-1) \pm 6(J+\frac{1}{2})^2 + v(J+\frac{1}{2}) \pm 2(J-\frac{1}{2})\}^2$ $\times [3u^{\mp}(J-1) \pm 2(J+\frac{5}{2})] - \omega(J+\frac{3}{2})u^{\mp}(J-1) \pm 2(J-\frac{1}{2})(J+\frac{1}{2}) - \lambda[(J-\frac{1}{2}) \pm 2(J-\frac{1}{2})u^{\mp}(J-1) \pm 2(J-\frac{1}{2})(J+\frac{1}{2})]^2$
$Q_{21}(J)$ $R Q_{32}(J)$	$Q_{21}(J)$ $P Q_{23}(J)$	$\frac{J+\frac{3}{2}}{8J(J+1)^2(J-\frac{1}{2})O^{\mp}(J)} \{(J-\frac{1}{2})(J+\frac{5}{2})u^{\mp}(J) \pm 6(J+\frac{1}{2})^2 + v(J+\frac{1}{2})[3u^{\mp}(J) \pm 2(J+\frac{5}{2})] \}^2$ $+ \omega[3(J-\frac{3}{2})(J+\frac{5}{2})u^{\mp}(J) \pm 2(J-\frac{1}{2})(J-\frac{1}{2})(J+\frac{3}{2}) - \lambda[\frac{3}{2}(J-\frac{1}{2})u^{\mp}(J) \pm (J-\frac{1}{2})(J+\frac{5}{2})]^2$
$R_{21}(J)$ $S R_{32}(J)$	$P_{21}(J+1)$ $O P_{23}(J+1)$	$\frac{(J+\frac{3}{2})(J+\frac{5}{2})}{16(J+1)^2(J+\frac{1}{2})O^{\mp}(J+1)} \{(J+\frac{5}{2})u^{\mp}(J+1) \pm 6(J+\frac{1}{2})^2 + v(J+\frac{1}{2})[3u^{\mp}(J+1) \pm 2(J+\frac{5}{2})] \}^2$ $- \omega[3(J-\frac{3}{2})u^{\mp}(J+1) \pm 2(J-\frac{1}{2})(J+\frac{1}{2}) + \lambda[(J-\frac{1}{2})u^{\mp}(J+1) \pm 2(J+\frac{1}{2})(J+\frac{5}{2})]^2$

Table 3.31 (continued)

$A'-A''$	$A''-A'$	${}^2\Pi'(\text{int})-{}^4\Pi(b)''$
${}^0P_{33}(J)$ $P_3(J)$	${}^S R_{33}(J-1)$ $R_3(J-1)$	$\frac{(J-3/2)(J-1/2)}{16J^2(J+1/2)C^{\mp}(J-1)} \{ (J-3/2)u^{\mp}(J-1) \pm 3(J+1/2)^2 - v(J+1/2)[3u^{\mp}(J-1) \pm 2(J-3/2)] \\ - \omega[3(J+5/2)u^{\mp}(J-1) \pm 2(J+1/2)(J+9/2)] + \lambda[(J+9/2)u^{\mp}(J-1) \pm 2(J-3/2)(J+1/2)] \}^2$
${}^P Q_{23}(J)$ $Q_3(J)$	${}^R Q_{32}(J)$ $Q_3(J)$	$\frac{J-1/2}{8J^2(J+1)(J+3/2)C^{\mp}(J)} \{ (J+3/2)((J-3/2)u^{\mp}(J) \pm 6(J+1/2)^2 - v(J+1/2)[3u^{\mp}(J) \pm 2(J-3/2)]) \\ + \omega[3(J-3/2)(J+5/2)u^{\mp}(J) \pm 2(J-1/2)(J+3/2)(J+9/2)] + \lambda[3/2(J+9/2)u^{\mp}(J) \pm (J-7/2)(J+3/2)] \}^2$
${}^Q R_{23}(J)$ $R_3(J)$	${}^Q P_{32}(J+1)$ $P_3(J+1)$	$\frac{J+5/2}{16J(J+1)(J+1/2)(J+3/2)C^{\mp}(J+1)} \{ (J+3/2)((J-3/2)u^{\mp}(J+1) \pm 6(J+1/2)^2 - v(J+1/2) \\ \times [3u^{\mp}(J+1) \pm 2(J-3/2)]) - \omega(J-1/2)[3(J-3/2)u^{\mp}(J+1) \pm 2(J+1/2)(J+9/2)] - \lambda[(J-1/2) \\ \times (J+9/2)u^{\mp}(J+1) \pm 2(J-3/2)(J+1/2)(J+3/2)] \}^2$
${}^N P_{24}(J)$ ${}^0 P_{34}(J)$	${}^T R_{42}(J-1)$ ${}^S R_{43}(J-1)$	$\frac{3(J-3/2)(J-1/2)(J+5/2)}{16J(J+1)C^{\mp}(J-1)} \{ (1-v+\omega-\lambda)[u^{\mp}(J-1) \pm 2(J+1/2)] \}^2$
${}^0 Q_{24}(J)$ ${}^P Q_{34}(J)$	${}^S Q_{42}(J)$ ${}^R Q_{43}(J)$	$\frac{3(J-1/2)(J+1/2)(J+5/2)}{8J(J+1)^2(J+3/2)C^{\mp}(J)} \{ (1-v)(J+3/2)[u^{\mp}(J) \pm 2(J+1/2)] - \omega[(J-3/2)u^{\mp}(J) \pm 2(J-1/2) \\ \times (J+3/2)] + \lambda[3/2u^{\mp}(J) \pm (J+3/2)] \}^2$
${}^P R_{24}(J)$ ${}^Q R_{34}(J)$	${}^R P_{42}(J+1)$ ${}^Q P_{43}(J+1)$	$\frac{3}{16(J+1)^2(J+3/2)C^{\mp}(J+1)} \{ (1-v)(J+3/2)(J+5/2)[u^{\mp}(J+1) \pm 2(J+1/2)] + \omega(J-1/2) \\ \times [(J-3/2)u^{\mp}(J+1) \pm 2(J+1/2)(J+5/2)] + \lambda(J+5/2)[(J-1/2)u^{\mp}(J+1) \pm 2(J+1/2)(J+3/2)] \}^2$

3.4. INTENSITY DISTRIBUTION FOR L-MULTIPLETS

As has been seen in Section 2.2, in certain cases, e.g., of light molecules, rotation not only de-couples the spin from the molecular axis (*Hund's* case *b*), but also initiates the de-coupling of the orbital angular momentum \vec{L} (transition from *Hund's* case *b* towards *d*). In the present section we shall deal with the intensity distribution of transitions between term complexes arising in this manner.

In the following, the spin will be totally neglected and the difference between *Hund's* cases *a* and *b* will thus be eliminated. Accordingly, the elements of the case *b* momentum matrix, serving as the starting point for our calculations (obtained by putting in (3.1-6) ψ_b , the case *b* eigenfunctions, in the place of ψ_a) can be calculated by (3.1-15) and (3.1-14), with the difference that in Table 3.1 in the line strength $S_{J'J''}$, A is substituted for Ω , and N for J , so that $S_{J'J''} \rightarrow S_{N'N''}$.

Assuming that there is only one electron outside the closed shell and assuming in addition the field to be central (hypothesis of pure precession) we obtain for the components of the electric transition-moment matrix given in (3.1-16)

$$\begin{aligned} |\int \Phi_{n',L',A'}^* \mathbf{M}_e \Phi_{n'',L'',A''} d\tau_e|^2 &= M_r^2(n',L'; n'',L' - 1) \delta_{A',A''} (L'^2 - A'^2) \\ |\int \Phi_{n',L',A'}^* \mathbf{M}_\eta \Phi_{n'',L'',A''} d\tau_e|^2 & \\ &= M_r^2(n',L'; n'',L' - 1) \delta_{A'',A'+1} \frac{1}{2} (L' \pm A') (L' \pm A' - 1) \end{aligned} \quad (1)$$

where

$$M_r(n',L'; n'',L' - 1) = - \frac{e}{\sqrt{4L'^2 - 1}} \int_0^\infty r P_{n',L'}^*(r) P_{n'',L'-1}(r) dr \quad (2)$$

and $P_{n',L'}(r)$ is the radial part of the electronic part of the molecular eigenfunction; it depends solely on the distance r of the electron from the origin of the coordinate system (Condon and Shortley [2]).

The intensities and line strengths calculated in this way agree, however, with experiment only if all terms involved in the transitions belong to *Hund's* case *b*. In the case of transitions belonging to the intermediate case between *Hund's* cases *b* and *d* we have to use the intermediate-case eigenfunctions ψ_R instead of ψ_b . The intermediate-case eigenfunctions can by Formula (1.5-4) be expressed as linear combinations of the case *b* eigenfunctions:

$$\psi_R = \sum_{A=0}^L S_{A,R} \psi_b^A \quad (3)$$

where the coefficients $S_{A,R}$ are the transformation-matrix elements calculated from (1.5-9), whose explicit forms for actual cases were already given in (2.2.2-4) and (2.2.3-5a, b).

Equation (3) yields the z component of the electric dipole moment:

$$R_z^{R'R''} = \int \psi_R^* \mathbf{M}_z \psi_{R''} d\tau \quad (4)$$



and using (1) the following expression is obtained instead of (3.1-15):

$$\sum_M |R_{n''v''N''}^{n'v'N'}|^2 = M_f^2(n', L'; n'', L' - 1) |R_{\text{vibr}}^{v'v''}|^2 \left| \sum_{A'=0}^{L'} S_{A', R'}^{N'} \delta_{A', A''} \sqrt{(L'^2 - A'^2)} \right. \\ \left. + \delta_{A'', A'+1} [(1 - |A'N|) A' - A'N] \sqrt{1/2 (1 + \delta_{0,A'}) (L' \pm A') (L' \pm A' - 1)} \right\} \\ \times \sqrt{3 \sum_{M=-N}^{+N} |L_{N''A''M}^{N'A'M}|^2 S_{A'', R''}^{N''}}^2 \quad (5)$$

where, in the summation with respect to M , $N = N'$ for emission, and $N = N''$ for absorption; furthermore, A means the smaller one of A' and A'' . Here it is the expression standing after $|R_{\text{vibr}}^{v'v''}|^2$ that corresponds to the line strengths $S_{R'R''}$. The explicit values of these will be given below for some actual cases.

If in (5) the transformation-matrix elements assume their case d forms, a new selection rule will hold $\Delta R = 0, \pm 1$.

3.4.1. p -Term Complex Transitions

By (3.4-1), in a transition between two terms, L is altered by unity. Therefore the simplest case is the change from $L = 1$ to $L = 0$. The first case is called p -term complex; the second is called s -term complex, although the latter case has only one Σ term. In the case of a p -term complex there may arise a $p\sigma\Sigma$ term and, by the twofold symmetry of the Π term, also a $p\pi\Pi_a$ and a $p\pi\Pi_b$ term. Table 3.32 lists the line strengths for the transitions between these terms and the term $s\sigma\Sigma$, according to (3.4-5).

Concerning $u^\pm(N)$ and $C^\pm(N)$ in Table 3.32, see (2.2.2-5); the exponent Σ_1 or Σ_2 is 0 or $+1$, according as the two Σ terms involved in the transition are Σ^+ or Σ^- . The notations $P(N)$, $Q(N)$, $R(N)$ refer to the changes by $+1, 0, -1$ of the case b rotational quantum number N ; the superfixes N, O, P, Q, R, S, T refer to the changes by $+3, +2, +1, 0, -1, -2, -3$ of the case d rotational quantum number R . The indication 'int' means that the terms in question are intermediate between *Hund's* cases b and d . The case b and d formulas can be obtained from these by putting $\alpha \rightarrow \infty$ in the first case and $\alpha = 0$ in the second case; $u^\pm(N)$ and $C^\pm(N)$ then assume the following values:

Case b $\alpha \rightarrow \infty$

$$u^+(N) = \alpha - 2$$

$$C^+(N) = 1/2(\alpha - 2)^2$$

$$u^-(N) = 0$$

$$C^-(N) = 2N(N + 1)$$

Case d $\alpha = 0$

$$u^+(N) = 2N$$

$$C^+(N) = 2N(2N + 1) \quad (1)$$

$$u^-(N) = 2(N + 1)$$

$$C^-(N) = 2(N + 1)(2N + 1)$$

Table 3.32. Intensity Distribution for the Transitions between p - and s -Complexes

$A'-A''$	$A''-A'$	$p\sigma\Sigma'(\text{int})-s\sigma\Sigma''$
$^oP(N)$	$^sR(N-1)$	$\frac{1}{2} [1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{N-1}{2C^-(N-1)} \{u^-(N-1) - 2N\}^2$
$^pQ(N)$	$^RQ(N)$	$\frac{1}{2} [1 - (-1)^{\Sigma_1+\Sigma_2}] \frac{2N+1}{2C^-(N)} \{u^-(N)\}^2$
$^qR(N)$	$^qP(N+1)$	$\frac{1}{2} [1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{N+2}{2C^-(N+1)} \{u^-(N+1) + 2(N+1)\}^2$
$p\pi\Pi'_b(\text{int})-s\sigma\Sigma''$		
$^pP(N)$	$^RQ(N-1)$	$\frac{1}{2} [1 - (-1)^{\Sigma_1+\Sigma_2}] (N-1)$
$^qQ(N)$	$^qQ(N)$	$\frac{1}{2} [1 + (-1)^{\Sigma_1+\Sigma_2}] (2N+1)$
$^RQ(N)$	$^pP(N+1)$	$\frac{1}{2} [1 - (-1)^{\Sigma_1+\Sigma_2}] (N+2)$
$p\pi\Pi'_a(\text{int})-s\sigma\Sigma''$		
$^qP(N)$	$^qR(N-1)$	$\frac{1}{2} [1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{N-1}{2C^+(N-1)} \{u^+(N-1) + 2N\}^2$
$^RQ(N)$	$^pQ(N)$	$\frac{1}{2} [1 - (-1)^{\Sigma_1+\Sigma_2}] \frac{2N+1}{2C^+(N)} \{u^+(N)\}^2$
$^sR(N)$	$^oP(N+1)$	$\frac{1}{2} [1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{N+2}{2C^+(N+1)} \{u^+(N+1) - 2(N+1)\}^2$

The formulas given in Table 3.32 have not been verified experimentally since this is the first time that they have been published. However, Bauer, Herzberg and Johns [12] observed a $3p$ -term complex- $^1\Sigma$ transition in the molecules BH and BD, but they did not give intensity values.

3.4.2. d -Term Complex Transitions

$L = 2$ yields the case of the d -term complex which gives rise to the terms $d\sigma\Sigma$, $d\pi\Pi_a$, $d\pi\Pi_b$, $d\delta\Delta_a$, $d\delta\Delta_b$. In Tables 3.33 and 3.34 the line strengths for the transitions from such a d -term complex to a p -term complex are given according to (3.4-5). Experiment has shown that in such transitions, the p -term complex is usually in a case b form. For this reason and also to avoid complicated formulas, line strengths will be given for transitions between a d -term complex intermediate between Hund's cases b and d and a case b p -term complex.

For the exponents Σ_1 and Σ_2 in Table 3.33 the same holds as in the previous cases. For the meaning in both tables of $u^\pm(N)$, $C^\pm(N)$ and $u_\Sigma^\pm(N)$, $u_\Delta^\pm(N)$, $C_\Sigma(N)$, $C_\Pi(N)$, $C_\Delta(N)$ cf. (2.2.3-6a) and (2.2.3-6b). Other notations are: $v_1 = v(N-1)$, $v_2 = v(N)$, $v_3 = v(N+1)$, where $v(N)$ is defined in (2.2.3-4).

The line strength formulas relating to the case *b* and case *d* form of the *d*-term complex can be obtained from the Table by putting $\alpha \rightarrow \infty$ and $\alpha = 0$, respectively. Then the above notations will assume the following meaning:

$$\text{Case b} \quad \alpha \rightarrow \infty \quad (1)$$

$$u^+(N) = 3(\alpha - 2), \quad u^-(N) = 0, \quad C^+(N) = \frac{9}{2}(\alpha - 2)^2, \quad C^-(N) = 2(N-1)(N+2)$$

$$u_\Sigma^+(N) = 2(\alpha - 2), \quad u_\Sigma^-(N) = 0, \quad C_\Sigma(N) = 12(\alpha - 2)^2 N(N+1)$$

$$u_\Delta^+(N) = 2(\alpha - 2), \quad u_\Delta^-(N) = 0, \quad C_\Delta(N) = 4(\alpha - 2)^2 (N-1)(N+2)$$

$$v(N) = 0, \quad C_\Pi(N) = 9(\alpha - 2)^2$$

$$\text{Case d} \quad \alpha = 0 \quad (2)$$

$$u^+(N) = 2(N-1), \quad u^-(N) = 2(N+2)$$

$$C^+(N) = 2(N-1)(2N+1) \quad C^-(N) = 2(N+2)(2N+1)$$

$$u_\Sigma^+(N) = 2(N-1), \quad u_\Sigma^-(N) = 2(N+1)$$

$$u_\Delta^+(N) = 2N, \quad u_\Delta^-(N) = 2(N+2)$$

$$v(N) = 2$$

$$C_\Sigma(N) = 8(N-1)(N+1)(2N-1)(2N+1)$$

$$C_\Delta(N) = 8N(N+2)(2N+1)(2N+3)$$

$$C_\Pi(N) = 12(2N-1)(2N+3)$$

Table 3.33. Intensity Distribution for the Transitions between *d*- and *p*-Complex e

$A'-A''$	$A''-A'$	$d\sigma\Sigma'(\text{int})-p\sigma\Sigma(b)''$
${}^N P(N)$	${}^T R(N-1)$	$\frac{1}{2} [1 + (-1)^{\Sigma_1 + \Sigma_2}] \frac{3(N-1)}{C_\Sigma(N-1)} [u_\Sigma^+(N-1)]^2 \{u_\Sigma^-(N-1) - 2N\}^2$
${}^o Q(N)$	${}^S Q(N)$	$\frac{1}{2} [1 - (-1)^{\Sigma_1 + \Sigma_2}] \frac{3(2N+1)}{C_\Sigma(N)} [u_\Sigma^+(N)u_\Sigma^-(N)]^2$
${}^P R(N)$	${}^R P(N+1)$	$\frac{1}{2} [1 + (-1)^{\Sigma_1 + \Sigma_2}] \frac{3(N+2)}{C_\Sigma(N+1)} [u_\Sigma^+(N+1)]^2 \{u_\Sigma^-(N+1) + 2(N+1)\}^2$

Table 3.33 (continued)

$A'-A''$	$A'-A'$	$d\pi\Pi'_b(\text{int})-p\sigma\Sigma(b)''$
${}^oP(N)$	${}^sR(N-1)$	$\frac{1}{2}[1 - (-1)^{\Sigma_1+\Sigma_2}] \frac{6(N-2)(N-1)(N+1)}{C^-(N-1)}$
${}^pQ(N)$	${}^RQ(N)$	$\frac{1}{2}[1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{6(N-1)(N+2)(2N+1)}{C^-(N)}$
${}^Q_R(N)$	${}^QP(N+1)$	$\frac{1}{2}[1 - (-1)^{\Sigma_1+\Sigma_2}] \frac{6N(N+2)(N+3)}{C^-(N+1)}$
$d\pi\Pi_a(\text{int})-p\sigma\Sigma(b)''$		
${}^PP(N)$	${}^RR(N-1)$	$\frac{1}{2}[1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{3(N-1)}{C_H(N-1)} (3-v_1)^2 \{(1+v_1)(\alpha-2) + 4N\}^2$
${}^QQ(N)$	${}^QQ(N)$	$\frac{1}{2}[1 - (-1)^{\Sigma_1+\Sigma_2}] \frac{3(2N+1)}{C_H(N)} (3-v_2)^2 (1+v_2)^2 (\alpha-2)^2$
${}^RR(N)$	${}^PP(N+1)$	$\frac{1}{2}[1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{3(N+2)}{C_H(N+1)} (3-v_3)^2 \{(1+v_3)(\alpha-2) - 4(N+1)\}^2$
$d\delta\Delta'_b(\text{int})-p\sigma\Sigma(b)''$		
${}^QP(N)$	${}^QR(N-1)$	$\frac{1}{2}[1 - (-1)^{\Sigma_1+\Sigma_2}] \frac{6(N-2)(N-1)(N+1)}{C^+(N-1)}$
${}^RQ(N)$	${}^PQ(N)$	$\frac{1}{2}[1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{6(N-1)(N+2)(2N+1)}{C^+(N)}$
${}^sR(N)$	${}^oP(N+1)$	$\frac{1}{2}[1 - (-1)^{\Sigma_1+\Sigma_2}] \frac{6N(N+2)(N+3)}{C^+(N+1)}$
$d\delta\Delta'_a(\text{int})-p\sigma\Sigma(b)''$		
${}^RP(N)$	${}^PR(N-1)$	$\frac{1}{2}[1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{3(N-1)}{C_A(N-1)} [u^-_A(N-1)]^2 \{u^+_A(N-1) + 2N\}^2$
${}^sQ(N)$	${}^oQ(N)$	$\frac{1}{2}[1 - (-1)^{\Sigma_1+\Sigma_2}] \frac{3(2N+1)}{C_A(N)} [u^-_A(N) u^+_A(N)]^2$
${}^TR(N)$	${}^NP(N+1)$	$\frac{1}{2}[1 + (-1)^{\Sigma_1+\Sigma_2}] \frac{3(N+2)}{C_A(N+1)} [u^-_A(N+1)]^2 \{u^+_A(N+1) - 2(N+1)\}^2$

Table 3.34. Intensity Distribution for the Transitions between d - and p -Complexes

$A'-A''$	$A''-A'$	$d\sigma\Sigma'(\text{int})-p\pi\Pi(b)''$
${}^N P(N)$	${}^T R(N-1)$	$\frac{3(N-1)(N+1)}{NC_{\Sigma}(N-1)} \{Nu_{\Sigma}^{+}(N-1) + (N-2)u_{\Sigma}^{-}(N-1) - u_{\Sigma}^{+}(N-1)u_{\Sigma}^{-}(N-1)\}^2$
${}^O Q(N)$	${}^S Q(N)$	$\frac{3(2N+1)}{N(N+1)C_{\Sigma}(N)} \{N(N+1)u_{\Sigma}^{+}(N) - (N-1)(N+2)u_{\Sigma}^{-}(N) + u_{\Sigma}^{+}(N)u_{\Sigma}^{-}(N)\}^2$
${}^P R(N)$	${}^R P(N+1)$	$\frac{3N(N+2)}{(N+1)C_{\Sigma}(N+1)} \{(N+1)u_{\Sigma}^{+}(N+1) + (N+3)u_{\Sigma}^{-}(N+1) + u_{\Sigma}^{+}(N+1)u_{\Sigma}^{-}(N+1)\}^2$
$d\pi\Pi'_b(\text{int})-p\pi\Pi(b)''$		
${}^O P(N)$	${}^S R(N-1)$	$\frac{3(N-2)(N-1)}{2NC^{-}(N-1)} \{u^{-}(N-1) - 2(N+1)\}^2$
${}^P Q(N)$	${}^R Q(N)$	$\frac{3(N-1)(N+2)(2N+1)}{2N(N+1)C^{-}(N)} \{u^{-}(N) - 2\}^2$
${}^Q R(N)$	${}^Q P(N+1)$	$\frac{3(N+2)(N+3)}{2(N+1)C^{-}(N+1)} \{u^{-}(N+1) + 2N\}^2$
$d\pi\Pi'_a(\text{int})-p\pi\Pi(b)''$		
${}^P P(N)$	${}^R R(N-1)$	$\frac{3(N-1)(N+1)}{NC_{\Pi}(N-1)} \{2N(3-v_1) - 2(N-2)(1+v_1) + (3-v_1)(1+v_1)(\alpha-2)\}^2$
${}^Q Q(N)$	${}^Q Q(N)$	$\frac{3(2N+1)}{N(N+1)C_{\Pi}(N)} \{2N(N+1)(3-v_2) + 2(N-1)(N+2)(1+v_2) - (3-v_2)(1+v_2)(\alpha-2)\}^2$
${}^R R(N)$	${}^P P(N+1)$	$\frac{3N(N+2)}{(N+1)C_{\Pi}(N+1)} \{2(N+1)(3-v_3) - 2(N+3)(1+v_3) - (3-v_3)(1+v_3)(\alpha-2)\}^2$
$d\delta A'_b(\text{int})-p\pi\Pi(b)''$		
${}^Q P(N)$	${}^Q R(N-1)$	$\frac{3(N-2)(N-1)}{2NC^{+}(N-1)} \{u^{+}(N-1) + 2(N+1)\}^2$
${}^R Q(N)$	${}^P Q(N)$	$\frac{3(N-1)(N+2)(2N+1)}{2N(N+1)C^{+}(N)} \{u^{+}(N) + 2\}^2$
${}^S R(N)$	${}^O P(N+1)$	$\frac{3(N+2)(N+3)}{2(N+1)C^{+}(N+1)} \{u^{+}(N+1) - 2N\}^2$

Table 3.34 (continued)

$A'-A''$	$A''-A'$	$d\delta A'_a(\text{int})-p\pi II(b)''$
${}^R P(N)$	${}^P R(N-1)$	$\frac{3(N-1)(N+1)}{N C_A(N-1)} \{N u_{\bar{d}}(N-1) + (N-2) u_{\bar{d}}^+(N-1) + u_{\bar{d}}^+(N-1) u_{\bar{d}}(N-1)\}^2$
${}^S Q(N)$	${}^O Q(N)$	$\frac{3(2N+1)}{N(N+1) C_A(N)} \{N(N+1) u_{\bar{d}}(N) - (N-1)(N+2) u_{\bar{d}}^+(N) - u_{\bar{d}}^+(N) u_{\bar{d}}(N)\}^2$
${}^T R(N)$	${}^N P(N+1)$	$\frac{3N(N+2)}{(N+1) C_A(N+1)} \{(N+1) u_{\bar{d}}(N+1) + (N+3) u_{\bar{d}}^+(N+1) - u_{\bar{d}}^+(N+1) u_{\bar{d}}(N+1)\}^2$

These results were verified (Kovács and Budó [123]) for the transitions $4d^3\Sigma-2p^3\Pi$, $4d^3\Pi_b-2p^3\Pi$, $4d^3\Pi_a-2p^3\Pi$, $4d^3\Delta_b-2p^3\Pi$, $4d^3\Delta_a-2p^3\Pi$ in the He_2 molecule against the measurements of Fujioka [54], where the upper states are intermediate between *Hund's* cases *b* and *d*, whereas the lower state belongs to *Hund's* case *b*, and the spin splitting is so small as to be totally negligible, wherefore the triplet terms can be treated as singlets. The theoretical and observed values were compared according to the third method described in Section 3.1, i.e. according to formula (3.1-24). The relative intensities of the lines belonging to the same upper rotational quantum number were formed in the following way:

$$\frac{P(N+1)}{P(N+1) + Q(N) + R(N-1)} \quad \frac{Q(N)}{P(N+1) + Q(N) + R(N-1)}$$

$$\frac{R(N-1)}{P(N+1) + Q(N) + R(N-1)}$$

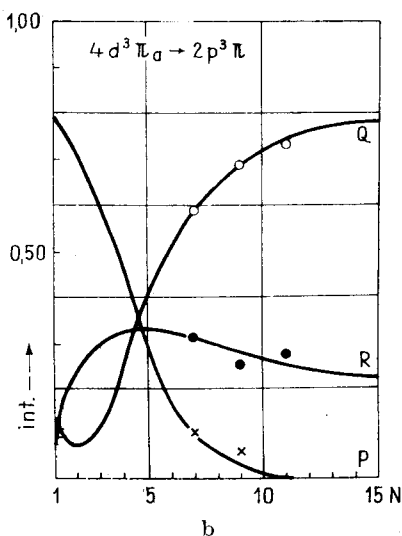
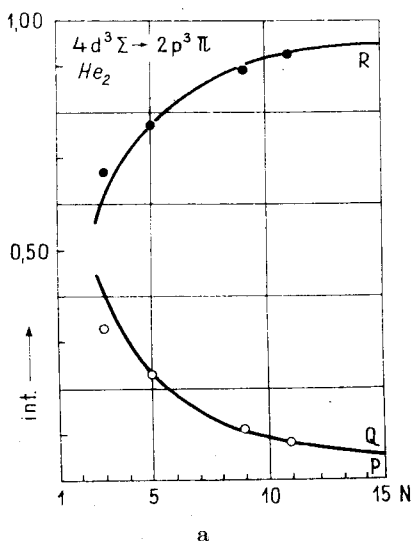


Fig. 3.10 (continued on p. 198)

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